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The effects of REDOX sensitive and insensitive chemical treatments on phosphorus release in sediments collected from hardwater eutrophic lakes.

By Kimberly L. Burley



A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Science

Department of Biological Sciences

Edmonton, Alberta

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THE UNIVERSITY OF ALBERTA
FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis titled, The effects of REDOX sensitive and insensitive chemical treatments on phosphorus release in sediments collected from hardwater eutrophic lakes, submitted by Kimberly L. Burley in partial fulfillment of the requirements for the degree Master of Science.

Abstract

The release of phosphorus (P) from bottom sediments is an important contribution to nutrient enrichment in many eutrophied lakes. Hardwater eutrophic lakes of the Boreal Plain in Alberta release P from bottom sediments during periods of seasonal anoxia, which implies that a reduction/oxidation (REDOX) sensitive mechanism regulates P release. REDOX sensitive and insensitive chemical treatments to control P release were tested in sediment cores collected from Amisk, Baptiste and Crooked lakes. REDOX potentials at the interface were related to P release from the cores ($P < 0.01$, $r^2 = 29-89\%$). Contrary to expectations, REDOX sensitive iron and/or oxygen treatments were no more effective in decreasing P release from the cores than were REDOX insensitive treatments lime and/or alum. As the fraction of P in sediment adsorbed and coprecipitated with iron and aluminum is low (non-apatite phosphorus fractions $< 5\%$), P release from these sediments is most likely controlled by apatite solubility and bacterial metabolism.

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1.0: Introduction:

A review of the literature on models of sediment phosphorus (P) release, chemical inactivation of sediment P release, and REDOX potential at the sediment-water interface

1.1 Background Information

1.1.1 Phosphorus (P)

The nutrient status and primary productivity of lakes are important classification criteria (Wetzel 1983). Over half of the lakes in the Alberta Boreal Plain and parkland are classified as eutrophic and commonly experience phytoplankton blooms (Mitchell and Prepas 1990). These lakes are often used for crop irrigation, livestock watering, and as a source of drinking water for humans. The phytoplankton blooms can pose serious health risks to humans, livestock and wildlife when they are dominated by toxin-producing cyanobacteria (Kotak et al. 1993). Microbial decomposition of the phytoplankton in the water column and at the sediment-water interface creates high biological oxygen demand (BOD), which decreases the oxygen available for fish and other benthic organisms (Barica 1975). Phytoplankton blooms may also create aesthetic problems for lakeshore residents and recreational users, including general unsightliness, bad taste and odor.

Phosphorus (P) is commonly the limiting nutrient for phytoplankton in fresh-water systems (Golterman 1977, Schindler 1977); reduction of lake P concentrations plays a key role in many lake reclamation projects (Cooke 1993, Prepas 1993). Phosphorus release from sediments has been implicated in delaying the recovery of lakes after nutrient diversion projects (Cooke 1993). On an annual basis, the major source of P to most lakes located in northern Alberta, is from the bottom sediments, i.e. internal P loading (Mitchell 1983, Riley and Prepas 1984, Mitchell and Prepas 1990, Shaw and Prepas 1990).

Internal P loading is regulated by chemical diffusion from bottom sediment, bioturbation (activities of organisms living in the sediment), and groundwater seepage (Mitchell and Prepas 1990, Shaw and Prepas 1990; Fig. 1.1). This investigation focuses on identifying the most effective methods for controlling P release from bottom sediments.

1.1.2 General Models of P Release

Sediment P release can be modeled through either mechanistic or empirical methods (Golterman 1991, Lijklema 1993). In the first approach thermodynamic constants and many measured parameters are used to model specific chemical and physical processes (Golterman 1991, Lijklema 1993, Seo and Canale 1996). These models are not only complex but many of the specific interactions are not known and are excluded from the models (Jorgensen et al. 1982, Golterman 1991, Lijklema 1993). Empirical models seek simple relationships between measured chemical parameters and observed macroscopic conditions (Golterman 1991, Lijklema 1993) and are not based on knowledge of processes. Although they lack theoretical insight (Golterman 1991, Lijklema 1993, Seo and Canale 1996), their predictive power can be high and they provide direction for the continued development of the mechanistic models (Lijklema 1993). Currently, many lake management decisions are based on empirical models because compared to the mechanistic models, they require fewer input data (Golterman 1991, Lijklema 1993, Seo and Canale 1996).

1.1.3 Empirical Models of P Release

Phosphorus release at the sediment-water interface has been studied by numerous authors and linked to a variety of factors. Two excellent review articles (Syers et al. 1973, Boström et al. 1982) summarize the work from

various lakes, and attempt to catalogue the parameters influencing P release. These include: REDOX potential (Eh) at the sediment-water interface (Mortimer 1941, 1942), oxic conditions (Prepas et al. 1990), bioturbation (Neame 1977), pH (Smayda 1990), iron availability (Lijklema 1976, Jackson and Schindler 1975), calcite adsorption and coprecipitation (Hieltjes et al. 1980), and temperature (Jensen and Andersen 1992). No single factor has been shown to reliably predict P release rates (Boström et al. 1982, Cooke 1993). The parameters thought to have the most influence on P release are REDOX potential, pH and temperature (Boström et al. 1982). An established relationship between REDOX potential at the sediment-water interface and sediment P release would allow lake managers to select effective treatments to inactivate sediment P release, and monitor conditions at the interface. The existence of this relationship would also necessitate the inclusion of REDOX potential in future mechanistic modeling.

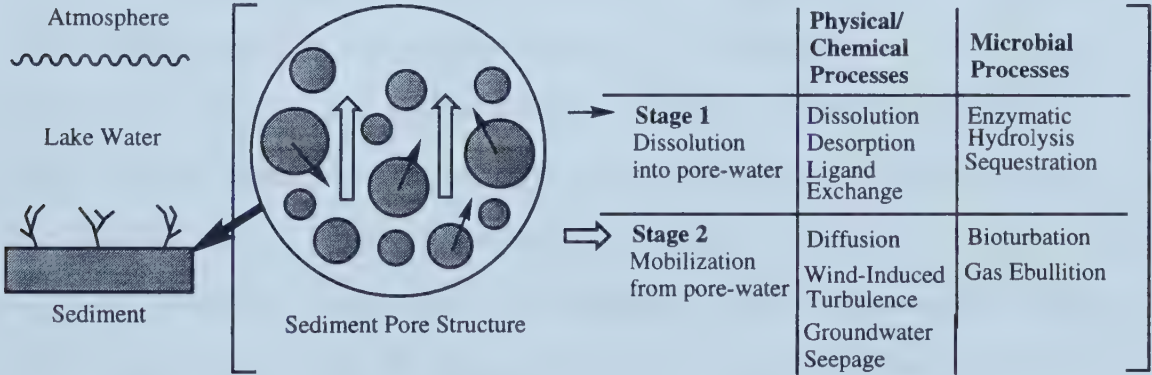


Figure 1.1: A two stage model of sediment phosphorus release from bottom sediment modified from the model proposed by Boström et al. (1982)

Mobilization of P from porewater is critical to the overall mass transfer of P, and is affected by a variety of physical factors. In the model presented by Boström et al. (1982), P is first dissolved into porewater by microbial and

physico-chemical processes, and then is mobilized from porewater by a second set of mechanisms (Figure 1.1). Since this model was proposed, other processes have been identified which merit addition to the model including: groundwater seepage (Shaw and Prepas 1990), the migration of biota between bottom sediments and the epilimnion (Brunberg and Boström 1992, Pettersson et al. 1993), and sequestration of particular ions by microbes (Eckerrot and Pettersson 1993)(Figure 1.1).

Sediment Chemistry Models of P Release

Boström and Pettersson (1982) used dredged sediments to determine three types of sediment P release patterns (Table 1.1). Reducing conditions were produced by adding acetate to stimulate bacterial O₂ consumption at the interface. Oxidizing conditions were produced by adding nitrate, which is an alternate electron acceptor and will stabilize REDOX potential at levels that prevent sulfate reduction. Sediments were classified as Type I if they exhibited no P release under either of the above conditions. Sediments classified as Type II behaved according to the classic theories of Einsele (1938) and Mortimer (1941, 1942), with P release under reducing conditions and no P release under oxidizing conditions. Type III sediments released P under both reducing and oxidizing conditions. Boström and Pettersson (1982) correlated the behaviours of the Type II and Type III sediments to the P fractions in the sediments determined by the extraction sequence modified from Hieljtes and Lijklema (1980). This fraction is commonly called the NAI-P fraction (nonapatite bound P) and represents the Al and Fe bound P in the sediment (Williams et al. 1971, Boström et al. 1982). The Type I sediments were too variable to be categorized in this way. Sediments that had a high proportion of nonapatite P (NAI-P) followed the Type II pattern. Type III sediments had very little P as NAI-P and

Boström and Pettersson (1982) suggested that apatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) systems dominated this sediment type.

Type III sediments release P through dissolution of hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) and calcite (CaCO_3) and take up P by coprecipitation with calcite, leading ultimately to the formation of hydroxyapatite (Boström et al. 1982). If sediment P release/sorption is regulated by calcite solubility, then REDOX conditions at the sediment-water interface have little impact on P release. In lakes where apatite bound P dominates the sediment P fraction, P regulation is thought to be linked to adsorption/desorption of P from calcite and the dissolution/formation of apatite (Avinmelech 1983, House 1990, Driscoll et al. 1993).

Recent studies that have explored the release of P from bottom sediments where apatite bound P dominates, have shown that a variety of factors affect the coprecipitation of P with calcite. Except in settled samples that contained too few precipitation nuclei, Danen-Louwerse et al. (1995) found a direct relationship between calcite precipitation and pH, which they called the Solubility Index (SI). Calcite precipitation is also influenced by calcium concentration ($\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$), and the concentration of P (Ishikawa and Ichikuni 1980, Avinmelech 1983, Danen-Louwerse et al. 1995).

Temperature may affect the solution kinetics by influencing rate. As well, microbes both in the water column and in the sediment may play a role in precipitation of P with calcite through their influence on the concentrations of both P and calcium. The microbes sequester calcium in their extracellular matrix, and may increase or decrease the concentration of P through metabolism (Brunberg and Boström 1992, Gächter and Meyer 1993).

Direct formation of apatite in natural environments is generally unlikely. The most likely mechanism is a three step process, in which dicalcium phosphate is formed, subsequently converted to octacalcium phosphate, and ultimately to hydroxyapatite (Grossl and Inskeep 1992). Adsorption of P on calcite is an important initial condition for this stepwise formation (Ishikawa and Ichikuni 1980, Avinmelech 1983, Grossl and Inskeep 1992). Danen-Louwerse et al. (1995) found that low P concentrations caused slow rates of incorporation (coprecipitation), and resulted in less formation of apatite.

Similar mechanisms are at work in the Type II bottom sediments, except P coprecipitation is associated with iron and aluminum complexes instead of calcite. The classic works of Einsele (1938) and Mortimer (1941, 1942) were the first to suggest this mechanism for regulation of P release from bottom sediment. Subsequent works have concentrated on finding specific mechanisms to explain the patterns put forward by Einsele and Mortimer. The majority of investigations center on the NAI-P fraction of sediment P, extracted according to Hieljtes and Lijklema (1980) with NH_4Cl and NaOH , or a subsequent modification of their technique. Danen-Louwerse et al. (1993) showed that for the NAI-P fraction, over 70% of the P sorption characteristics of sediment can be fitted to a Langmuir isotherm and therefore are explained by a classic adsorption model. When NAI-P dominates, the sediments are sensitive to changes in both REDOX and pH (Boström et al. 1982, Danen-Louwerse et al. 1993). In Type II sediments, under oxic conditions, iron III hydroxides precipitate from the water column and act as sorption sites for P in the water column (Stumm and Morgan 1981). The precipitated iron III hydroxides and oxides act as a cap on the sediment-water interface, thus

preventing P mobilization from the sediments (Mortimer 1941, 1942, Stumm and Morgan 1981). When iron is reduced at the interface, the coprecipitated and adsorbed P is released as iron II compounds are dissolved into the water column (Mortimer 1941, 1942). Thus, Type II sediment P release is regulated by the oxidation state of iron in the sediment and the water column.

The previous studies have used several methods and focused on a variety of bottom sediments, under a wide range of conditions. Although the range of sediment compositions and conditions can be detrimental to reaching a mechanistic picture of the sediment-water interface, some very useful generalizations can be made. Sediment P release is dependent upon a process, physico-chemical or microbial, that will mobilize P from the solid phase. Phosphorus is first released into porewater, and then transported from porewater into the water overlying the sediment. Conditions leading to sediment P release vary according to the sediment composition and are influenced by the iron, calcium, aluminum and organic content of the sediment. The mineral types within the sediment are expected to predict the conditions which would lead to the greatest sediment P release. The NAI-P, which includes P both bound and sorbed to iron and aluminum, is the fraction of the sediment that is most susceptible to REDOX condition. As well, this mineral type is affected by pH increases above 6 (Jensen and Anderson 1992, Danen-Louwerse et al. 1993). The P adsorbed on calcite and in apatite and hydroxyapatite is thought to be insensitive to REDOX changes and only sensitive to pH changes between 8-10 and again at pH >12 (Böers 1991). Temperature has a profound effect on solution kinetics and could be important in nearshore sediments and during mixing in the profundal sediments (Ryding 1985).

1.1.4 REDOX Potential and the Platinum Electrode

Mortimer, (1941,1942) was first to demonstrate that the REDOX potential in the vicinity of the sediment-water interface may control the rate of P release. Since that time, REDOX studies have attempted to identify the specific ionic species that may be involved in regulating nutrient release (Cole 1975, Hostettler 1984, Davison 1985, Morgan and Stone 1985, Sholkovitz 1985). Although the geochemistry of the sediment-water interface is poorly understood, a strong relationship between REDOX potential and P release would provide lake managers with a valuable indicator for assessing treatment effects in lakes where the bulk of the P is recycled from Type II sediments (NAI-P dominated).

Platinum electrodes are commonly used to measure REDOX potential; however some questions have been raised regarding their reliability and validity. Specifically, there is uncertainty as to what the potential of the electrode represents, and how reliable over time they are in the natural environment (Whitfield 1969, 1974, Bohn 1971, Mortimer 1971, Stumm and Morgan 1981, Hostettler 1984, Stumm, Morgan and Hostettler 1985). Consensus exists that the potential of the platinum electrode represents the total reduction-oxidation conditions found at a particular site (Bohn 1971, Mortimer 1971, Stumm and Morgan 1985). No specific REDOX couple is thought to drive this potential at the sediment-water interface where the chemical and physical environment changes rapidly on a fine temporal and spatial scale. Trends in REDOX potential at the sediment-water interface reflect changes in a pool of electron donors and acceptors and may be used to infer possible bacterial roles in the generation of certain reduced species (Stumm and Morgan 1981, Forster and Graf 1992, Jensen and Andersen 1992).

The reliability of platinum electrodes is an important issue. Many authors have listed a number of quality control issues (Bohn 1971, Mortimer 1971, Stumm and Morgan 1981, Hostettler 1984). Mortimer (1971) best outlines the problem and lists the following considerations for using the platinum electrodes:

- 1) mechanical disturbance;
- 2) drift over time;
- 3) reproducibility;
- 4) electrode contamination by sulfides;
- 5) electrode area;
- 6) mixed potentials preclude rigorous physico-chemical interpretation.

1.1.5 Treatment Background

As the mechanisms of P release at the sediment-water interface have begun to be understood, research has started to focus on controlling and altering sediment P release. Decreases in P loading to the euphotic zone of some eutrophic lakes have been accomplished by the application of lime (Prepas et al. 1990, Murphy and Prepas 1990, Babin et al. 1994), oxygen (Jaeger 1994, Prepas et al. 1997), alum (Cooke et al. 1993) and iron (Cooke 1993, Böers et al. 1994). The success of these treatments has been attributed to the decrease in phosphorus transfer from the bottom sediment (Cooke 1993, Böers et al. 1994).

The various treatments interact differently with the sediment-water interface (Stumm and Morgan 1981, Cooke 1993). Oxygen treatments push the oxidized layer deeper into the sediment, which raises the oxidation potential at the sediment-water interface. This creates a thick oxidized layer in the sediment,

which acts as a P transfer barrier due to its impact on iron solubility (Cooke 1993). Iron treatments increase P retention in sediment by adding coprecipitation and adsorption sites (Cooke 1993). Treatments employing oxygen, iron or combinations of both increase the oxidation potential at the sediment-water interface.

Lime and alum treatments should not affect the REDOX boundary. Enhanced P binding at the sediment-water interface is thought to be attributable to coprecipitation/adsorption mechanisms with calcium compounds (Cooke 1993). Lime treatments reduce sediment P release by adding calcite content to the sediment which provides additional P adsorption sites and binding P directly through the formation of apatite (Avinmelech 1980, Grossl and Inskeep 1992, Danen-Louwerse et al. 1995). According to Grossl and Inskeep (1992), lime treatments have their greatest effect in sediments where P inactivation is regulated by calcite precipitation leading to the formation of hydroxyapatite. These sediments are classified as Type III sediments in Boström and Pettersson's (1982) model. Alum reduces P release from sediments by adding mineral content to the sediment which provides additional P adsorption sites ($\text{Al}(\text{OH})_3$; Kuo et al 1988, Van Benschoten et al 1990). Alum can bind P directly, but more commonly adsorbs considerable amounts of P onto aluminum oxides and hydroxides (Cooke 1993). The flocculant layer on the sediment surface forms a barrier against diffusion of dissolved P from the interstitial water. The solubility of the Al-P compounds depends upon pH. Therefore inactivation of sediment P by alum treatment should be effective across all sediment types providing the pH stays within the appropriate range (> 6). In addition to their P binding mechanisms in bottom sediment, both alum and lime may reduce

water column P by flocculation of particulates and by providing P adsorption sites (Cooke 1993).

1.2 Objectives

The objectives of this study were to:

- 1) determine which treatments (REDOX sensitive or insensitive) would be most effective in decreasing P release from bottom sediments;
- 2) determine if REDOX potential at the sediment-water interface would predict sediment P release from bottom sediments.

Experiments were conducted with sediment cores collected from three eutrophic hardwater lakes. These lakes all have a high proportion, (estimated by mass balance), of their annual phosphorus load from bottom sediments (Prepas 1990a, Prepas 1990b, Prepas unpublished). Sediment cores from the three lakes were used as a microcosm of the sediment-water interface.

Table 1.1: Overview of phosphorus (P) release mechanisms proposed in the literature, classified by sediment chemistry¹

Sediment Type	P-Fraction	Proposed Chemistry	Stage 1 Mechanisms	P-Release Factors
¹ Type I: no release under oxidizing or reduced conditions	NA	NA	NA	NA
¹ Type II: release under reducing but not oxidizing conditions	² NaOH/NH ₄ Cl extraction (nonapatite - P)	³ coprecipitation with Fe and Al complexes	⁵ Fe and Al complex solubility; Langmuir adsorption isotherm	⁶ pH ⁶ REDOX
¹ Type III: release under both oxidizing and reducing conditions.	² acid extractable P Apatite - P	⁴ coprecipitates with CaCO ₃ (calcite) or Ca ₅ (PO ₄) ₃ OH (apatite)	⁴ Solubility of calcium minerals.	⁷ pH ⁷ temperature

Note:

NA, not applicable

¹Boström and Pettersson (1982)

²Böers (1991); Boström and Pettersson (1982)

³Einsele (1938); Mortimer (1941, 1942); Williams (1971); Hieljtes and Lijklema (1980); Boström (1982)

⁴Grossl and Inskeep (1992); Danen-Louwerse et al. (1993); Flemming (1995)

⁵Danen-Louwerse et al. (1993)

⁶Hassleman et al. (1950); Boström et al.. (1982); Jensen and Anderson (1992); Danen-Louwerse et al. (1993)

⁷Danen-Louwerse et al. (1995)

⁸Ryding (1985)

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Chapter 2.0

The effects of REDOX sensitive and insensitive chemical treatments on phosphorus release in sediments collected from hardwater eutrophic lakes.

2.1: Introduction

Phosphorus (P) is often the nutrient limiting the growth of algae and aquatic plants in fresh-water systems (Golterman 1977, Schindler 1977). Nutrient enrichment of fresh water poses severe problems for natural ecosystems world-wide. Even when external sources of P loading decrease, internal recycling of P from bottom sediments can sustain eutrophication within a watershed (Welch and Cooke 1995, Böers et al. 1998, Harremoës 1998).

Ultimately, control of eutrophication will depend on the ability to remove P from the ecosystem or stabilize it in the sediment (Welch and Cooke 1995, Böers et al. 1998).

Recycling of P from the sediments to the water-column is often modeled as a two-stage process. The first step is dissolution of sediment-bound P into porewater, which is then followed by mobilization from porewater into the overlying water (Boström et al. 1982). Dissolution of P into porewater has traditionally been described as dependent on oxidation potential (REDOX), and regulated by iron chemistry (Mortimer 1941, 1942, Lijklema 1976). Caraco et al. (1993) modified Mortimer's classic iron model by proposing that iron cycling was actually controlled by sulfate reduction cycles and the formation of pyrite (FeS). When Fe is bound in pyrite it is not available to adsorb or bind P which lowers the sediment's capacity to hold P out of the water column. In addition to the iron precipitation models, polyphosphate metabolism by microbes has been proposed as a mechanism to explain the REDOX dependence of sediment P release (Eckerrot and Pettersson 1993, Waara et al. 1993, Gächter and Meyer

1995). Boström and Pettersson (1982) grouped sediments into three types according to their REDOX sensitivity: Type I sediments are REDOX insensitive and do not release P; Type II sediments are REDOX sensitive and release P under anoxic conditions (low oxidation potential), and by dissolution of P bound to iron and aluminum compounds in the sediment; Type III sediments are REDOX insensitive and release P as a function of apatite solubility. The Boström and Pettersson (1982) model builds upon the classic iron models of sediment P release and yet incorporates REDOX insensitive P release.

Because P release from lake sediments can be REDOX dependent or independent, a variety of treatments to control internal P loading have been employed in productive lakes worldwide (Cooke 1993). Treatments with lime and/or alum are REDOX insensitive and should be most effective in lakes where sediment P release is REDOX insensitive, Type III sediments. Lime and alum act by forming precipitates in the water column, which then settle on the sediment surface (Cooke 1993). The precipitates trap P in the water column and act as surfaces for adsorption and coprecipitation of P that may mobilize from bottom sediments (Avinamelech 1983, Grossl and Inskeep 1992, Cooke 1993). In contrast, oxygen and/or iron treatments are REDOX sensitive and increase oxidation potentials at the interface and, in the case of iron, also provide increased adsorption and/or coprecipitation surfaces for P in the sediment (Cooke 1993, Boers et al. 1994). Despite the theoretical potential to predict treatment effectiveness in controlling eutrophication by internal P release, there are few cases where sediment REDOX sensitivity has been measured prior to lake treatment.

In this study, the effectiveness of lime, alum, oxygen and iron treatments in decreasing P release from intact sediment cores will be compared as a function of REDOX potential at the sediment-water interface. Sediment cores were obtained from eutrophic lakes situated on the P-rich glacial till in northern Alberta, Canada (Mitchell and Prepas 1990). In these lakes, anoxia (low oxidation potentials) at the sediment-water interface is associated with the release of large quantities of P from bottom sediments (Riley and Prepas 1984, Mitchell and Prepas 1990, Shaw and Prepas 1990). However, the Fe mechanism (i.e. Type II) proposed by Boström and Pettersson (1982) does not seem to apply, as these lakes are low in available iron in the water column (Mitchell and Prepas 1990) and the dominant Fe fraction in the sediment is insoluble pyrite (Manning et al. 1994, in press). Systematic laboratory tests of a range of REDOX sensitive and insensitive chemical treatments on a single set of sediments have not previously been recorded (Welch and Cooke 1995, Böers et al. 1998). The unique characteristics of P-release under anoxic conditions yet low concentrations of available iron in these lakes provide an ideal opportunity to investigate REDOX effects on P release and discriminate these effects from adsorption/coprecipitation with iron.

2.2: Methods

Study Sites

Bottom sediments were collected from three hardwater, eutrophic lakes in north-central Alberta: Crooked Lake (54°55'N 113°33'W), the north basin of Amisk Lake (54°35'N 112°37'W), and the north basin of Baptiste Lake (54°45'N 113°33'W). All three lakes are classed as eutrophic to hypereutrophic based on both chlorophyll *a* and mean total phosphorus (TP) concentrations and all release P during seasonal anoxia (Table 2.1). The three lakes have hardwater with well-buffered water columns (Prepas and Burke 1997, Reedyk et al. in press). Crooked Lake has not been chemically treated within the known history of the lake. Baptiste Lake was treated with sulfuric acid in 1945 in an attempt to control *Triaenophorus*, a tapeworm parasite of cisco, however, the pH of the water column was not affected (Miller and Watkins 1946). The hypolimnion of the north basin of Amisk Lake was aerated with oxygen for 5 years (1988-1993) prior to this study (Prepas et al. 1997a). Sediment cores were collected in the summer of 1994, one year after the aeration with O₂ ceased, and O₂ concentrations had returned to pre-treatment levels (Aku et al. 1997).

Field Data

During 1993, measurements of water quality were collected for ongoing studies of the *in situ* effectiveness of treatments with either oxygen gas (O₂) (Prepas and Burke 1997), or lime (Reedyk et al. in press). Data that were used from Amisk Lake during June-August of 1993 were from the final year of O₂ treatment to the hypolimnion. For comparison with pretreatment, dissolved oxygen (DO) and TP concentrations were included from 1980-85 (Prepas and Burke 1997). Concentrations of total phosphorus (TP), dissolved oxygen (DO), nitrites and nitrates (NO₂⁻+NO₃⁻), ammonium (NH₄⁺), sulfate (SO₄²⁻), pH and,

calcium (Ca^{2+}) were measured for water samples collected in the hypolimnion, 1-m above the sediment-water interface at the deepest point in the lake. Further details on methodology are given in Prepas and Burke (1997) or Reedyk et al. (in press). Regression analysis was used to quantify relationships of hypolimnetic TP concentrations to DO, $\text{NO}_2^- + \text{NO}_3^-$, NH_4^+ , SO_4^{2-} , pH, and Ca^{2+} in the water chemistry data from the summer of 1993, and also with DO for 1980-85 in Amisk Lake.

Laboratory Experiments

a) Design

Sixteen sediment cores (21-cm long) were collected with a four-barrel corer from the deepest location in each of Baptiste and Crooked lakes in July. In August, sixteen cores were collected from Amisk and Crooked lakes, and eighteen were collected from Baptiste Lake. Cores were capped and sealed in the field, packed in ice, and transported to the laboratory within 6 h. Cores were maintained in environmental chambers in the dark at 10°C for the duration of the experiment. An array of three platinum electrodes was inserted into the sediment-water interface (Figure 2.1). A silver/silver chloride (Ag/AgCl) reference electrode was suspended in the water column. A syringe was attached to Tygon[®] tubing that acted as a pressure release valve during the experiment. Gas treatments were delivered through another Tygon[®] tube that passed through the sealed cap and ended with an aeration stone. Core tubes had three syringe sampling ports drilled at heights of 0.5, 2.5 and 5 cm above the sediment-water surface and sealed with clear silicon caulking. The ports allowed water overlying the sediment to be sampled for water chemistry without disturbing the water column.

REDOX potentials (Eh) were measured by an array of platinum electrodes (Mortimer 1941, 1942, 1971, Smayda 1990, Jensen and Andersen 1992), and a Ag/AgCl reference electrode (Farrell et al. 1990). The platinum electrodes were constructed from 0.5-mm diameter platinum wire soldered to copper wire (Figure 2.1). Three electrodes were then fashioned into an array with 1-cm spacings to allow monitoring of REDOX potential 1-cm above, 1-cm below and at the sediment-water interface (Figure 2.1). The electrode system was standardized in Light's (1972) standard solution after construction and prior to use. Multichannel data were stored from each electrode array, on a Campbell Scientific CR10[®] datalogger with a multiplexer attachment. REDOX potential was measured for each electrode in the array every 15 minutes and 12-h means were calculated at 1200 and 2400 h by the datalogger.

The electrode and experimental designs described here controlled for most of the concerns surrounding the use of platinum electrodes described by Mortimer (1971). However, contamination of the electrodes by sulfides can occur when the electrodes are left in place over a long time. High sulfide generation is known to occur in Amisk and Baptiste lakes (Manning et al. 1994, in press) and may also occur Crooked Lake (K. Burley personal observation). Tests of the effects of sulfide poisoning *in situ*, confirmed that the electrode potentials were stable and accurate under the environmental conditions of the laboratory experiments (Appendix A).

To establish anoxia, the water overlying the cores was bubbled with nitrogen gas (N₂) for two days prior to the experiments. Eight treatments were applied to duplicate cores from each lake. Duplicate cores from each lake received one of six experimental treatments: alum, lime, lime+alum, iron III chloride

(FeCl₃), oxygen (O₂), FeCl₃+O₂ (Table 2.2), or one of two reference conditions N₂ gas alone, or N₂ bubbling accompanied with diatomaceous earth (D.E.). D.E. was included to simulate the effects of a simple physical barrier to diffusion, without the additional P adsorption properties of the flocculant treatments. In the August trial, the two extra cores from Baptiste Lake were bubbled with nitrogen and stored in the environmental chamber. Except for O₂ treatments, cores receiving the experimental treatments were also continuously bubbled with N₂. Other than the gas treatments, all doses were calculated as a mass per unit of surface area of the cores. Solid chemical treatments were administered by withdrawing approximately 25-30 mL of water from the 5-cm sample port, mixing in the powdered chemical to make a dilute slurry, and then injecting the slurry back into the water column 5-cm above the sediment-water interface. Lime and alum treatments are known to impact pH (Cooke 1993) and were administered slowly to control for this effect. Treatments with FeCl₃ were administered in a single dose and no attempt was made to control pH. Care was taken during treatment and sampling to avoid disrupting the sediment-water interface.

The experiments ran for 21 days. Water samples for chemical analyses were withdrawn by syringe from the sampling port at 0.5-cm, for initial conditions, and 2.5-cm above the sediment-water interface for the post-treatment samples to avoid disturbing the flocculant layer in the treated cores. Total phosphorus (TP) was measured pre-treatment (TP_i), and on days 7, 14 and 21 (TP_f) post-treatment. To minimize the volume of water removed during the experiment, soluble reactive phosphorus (SRP) concentration and pH were only measured pre-treatment (SRP_i, pH_i) and at the end of the trial (SRP_f, pH_f). TP concentrations were analyzed after Menzel and Corwin's (1965) potassium

persulfate digestion method as modified by Prepas and Rigler (1982) on duplicate 5-mL samples that were diluted to 25-mL with distilled deionized water. Similarly diluted samples were analyzed for SRP by Murphy and Riley's (1962) method. pH was measured with a portable Beckman 10 pH meter. At the end of the trial DO was measured on a 10-mL sample with a microWinkler technique (Burke 1962). Only, TP data were collected from the water column for the two extra cores collected from Baptiste Lake.

At the end of each trial, the sediments from the N₂ reference cores were extruded and sliced at 2-cm intervals, homogenized, placed in Ziploc[®] bags and frozen for chemical analyses. The two additional cores, collected in August from Baptiste Lake, were included in the sediment analyses with the N₂ reference cores from both trials (Amisk $n=2$, Baptiste $n=6$, Crooked $n=4$). The top two surface slices (0-4 cm) were combined to ensure sufficient sample volume for analysis. Duplicate sub-samples of each slice were analyzed for water content (%), and exchangeable NaOH-P after Williams et al. (1976). Total phosphorus in sediment (TP), total iron (Fe_S), and total calcium (Ca_S) were also measured on sub-samples of the surface slices by atomic absorption spectrophotometry.

Data Analyses

To test for differences amongst lakes and amongst treatments, ANCOVA's were performed on the final concentrations of TP (TP_f) and SRP (SRP_f), and final pH (pH_f) with initial TP (TP_i), SRP (SRP_i), or pH (pH_i) as a covariate. TP release rate (RR) expressed as $\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ was determined for each core as the slope of concentration versus time regression for TP values measured on days 7, 14 and 21. DO concentrations, and RR were analyzed by ANOVA to determine

differences among treatments and among lakes. Fischer's LSD *post hoc* test was used in all cases to determine differences between alum, FeCl₃, lime, O₂, the combination treatments and the two reference conditions (N₂ alone and with D.E.).

REDOX potentials (Eh) were analyzed graphically over time, and by ANCOVA performed on the final potentials (Eh_f) with initial potential (Eh_i) as the covariate. Potentials were plotted over time for each electrode in each core. The potentials at the interface showed the greatest change over time and were selected to represent the REDOX conditions affecting P release. As pH varied among treatments, Eh_i and Eh_f were corrected to a standard pH of seven by the addition/subtraction of 57 mV for each unit decrease/increase from seven (Smayda 1990 based on Pearsall's (1938) equation). The oxidation potentials were also corrected for the potential of the Ag/AgCl electrode to the standard hydrogen electrode by the addition of 244 mV. To determine if pH_f or Eh_f were predictive of P release, stepwise regressions were performed relating RR, log SRP_f or log TP_f to final Eh_f and pH for the various chemical treatments (*alpha* level set at 0.05 for inclusion of each term). Total phosphorus RR data were not log transformed as RR was normally distributed and variance was homogeneous when examined graphically. TP_f and SRP_f concentrations were log transformed to log₁₀ for comparison to final Eh_f to homogenize variance and normalize the distribution.

To determine if RR is affected by iron concentrations of the sediment (Fe_s), the iron to phosphorus ratio of the sediments (Fe_s:TP) was calculated for the N₂ reference treatments and compared by regression to the total phosphorus RR calculated for those same cores (Lijklema 1976, Jensen et al. 1992). Also, a

regression of \log_{10} RR versus \log_{10} TP in sediment was calculated, and the coefficient of determination (r^2) was compared qualitatively to that of Nürnberg (1988) for lakes on the Canadian Shield. To determine if RR was correlated with apatite in sediments (i.e. Type III sediments, Boström and Pettersson 1982), RR was regressed against the concentration of calcium in sediment (Ca_s). All statistical analysis of the data were performed with the Systat 5.2.1[©] statistical package for Macintosh[®] computers. All statistical analyses were held to an *alpha* level of 0.05 to determine significance.

Table 2.1: Limnological data for Amisk, Baptiste and Crooked lakes. Whole-lake surface area (A_0), mean basin depth (z), maximum basin depth (z_{max}), whole lake drainage basin area (A_d), mean summer total phosphorus (TP_m) $\pm SE$, mean summer chlorophyll a (Chl_a) $\pm SE$, total phosphorus release rate (RR), and water residence time (T_w), are reported as in Prepas (1990a[†], 1990b^δ), and Reedyk et al. (in press^ψ).

Lake	A_0 (km^2)	z (m)	z_{max} (m)	A_d (km^2)	TP ($\mu g \cdot L^{-1}$)	Chl a ($\mu g \cdot L^{-1}$)	RR ($mg \cdot m^{-2} \cdot d^{-1}$)	T_w (y)
Amisk L. [†] (N. Basin)	2.33	10.8	34	234	32 \pm 2.0 ^q	17 \pm 1.6 ^q	6.2 ^z	8
Baptiste L. ^δ (N. Basin)	5.07	5.6	15.5	288	54 \pm 10.9 ^r	30 \pm 10.3 ^r	11 ^s	6
Crooked L. ^ψ	2.38	4.1	9.0	146	64 \pm 6.1 ^w	20 \pm 2.9 ^w	4.3 ^u	7

q composite samples of euphotic zone collected 1987

r composite samples of euphotic zone collected 1986

s summer release rate pooled for 1980-1987

t summer release rate 1982

u summer 1992

w summer 1993

Table 2.2: Treatment doses and the rationale for the dosage for each core in the experimental and reference groups. Combined treatments were a combination of the single doses.

<u>Treatment</u>	<u>Dosage</u>	<u>Rationale</u>
Alum $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$	$13 \text{ g Al}^{3+} \cdot \text{m}^{-2}$	-half of dose administered to surface of West Twin Lake OH (dimictic alkaline lake (Cooke 1993)
Lime $\text{Ca}(\text{OH})_2$	$140 \text{ g Ca}^{+} \cdot \text{m}^{-2}$	-highest dose administered to similar lake water (Babin et al. 1994, Prepas et al. 1997b)
Iron III Chloride FeCl_3	$100 \text{ g Fe}^{3+} \cdot \text{m}^{-2}$	-same dose as administered by Böers et al. (1994) and Quaak et al. 1993)
Oxygen* O_2	$220 \text{ mL} \cdot \text{min}^{-1}$	-average rate of flow to maintain positive pressure in system
Diatomaceous. Earth D.E.	$200 \text{ g} \cdot \text{m}^{-2}$	-chosen to provide same total mass as lime treatments
Nitrogen* N_2	$150 \text{ mL} \cdot \text{min}^{-1}$	-average rate of flow to maintain positive pressure in system

*Gases were delivered continuously throughout experiment.

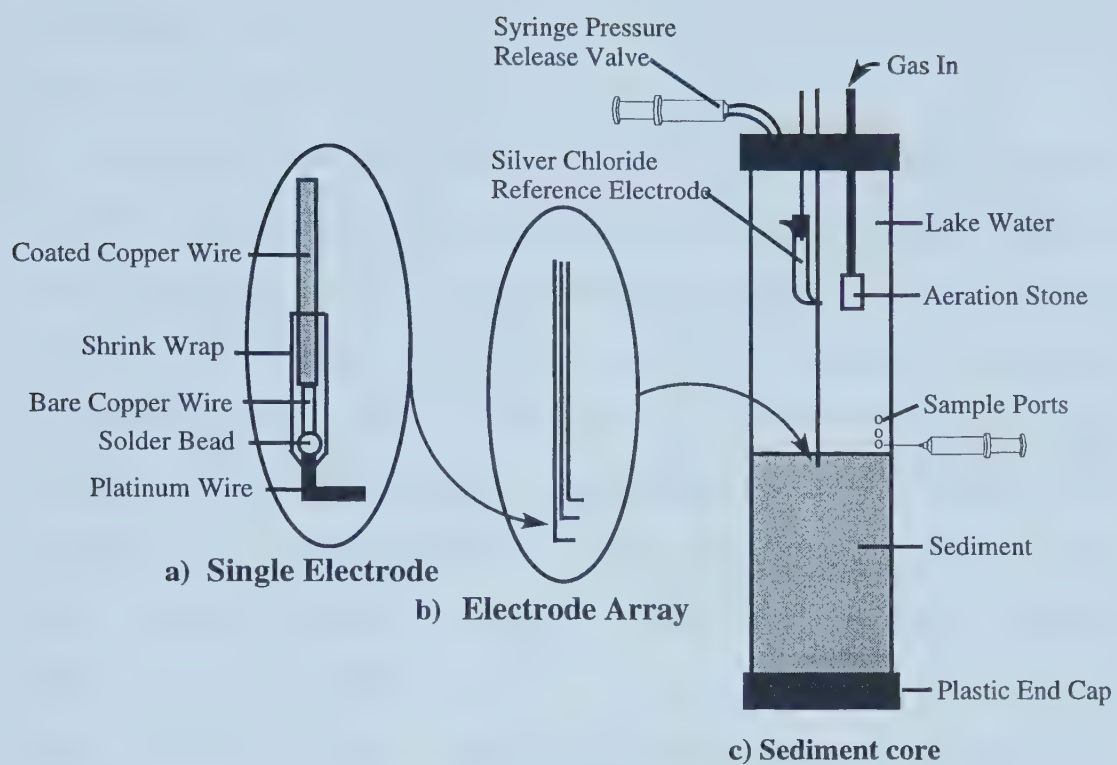


Figure 2.1: Experimental set-up showing: a) electrode design, b) electrode array, and c) sediment core.

2.3: Results

Field Measurements

TP concentrations in the in the bottom 1-m of the hypolimnion increased when DO concentrations decreased for all three lakes (Table 2.3). Trends in the water chemistry data for all three lakes from the summer of 1993 were in the same direction, however not all relationships were significant. In addition to the relationship with DO, TP concentrations in the hypolimnion of Crooked Lake were correlated to the REDOX related chemical species, $\text{NO}_2^- + \text{NO}_3^-$, SO_4^{2-} (negatively), and NH_4^+ (positively). Additionally, TP concentrations were related negatively to pH and positively to Ca^{2+} concentrations in Crooked Lake. Relationships between TP and pH or Ca^{2+} were consistent with P release from apatite in bottom sediments. In the bottom water of Baptiste Lake, TP concentration was negatively correlated with the concentration of one other REDOX related chemical species, SO_4^{2-} , but not with $\text{NO}_2^- + \text{NO}_3^-$ ($P=0.40$, $n=6$). TP and pH were negatively correlated in the hypolimnion of Baptiste Lake, which suggested some regulation of P release by apatite. However, TP and Ca^{2+} concentrations were not related ($P=0.35$, $n=10$). In Amisk Lake, TP concentration was only sensitive to $\text{NO}_2^- + \text{NO}_3^-$, and was not related to SO_4^{2-} ($P=0.20$, $n=10$), pH ($P=0.15$, $n=9$), or Ca^{2+} ($P=0.13$, $n=10$). Amisk Lake was treated with O_2 throughout the summer of 1993, which would explain the dominance of REDOX sensitive TP relationships. TP concentrations in Baptiste and Crooked lakes were related to both REDOX and apatite sensitive compounds.

Laboratory Experiments

Three of the six chemical treatments to sediment cores from Amisk, Baptiste and Crooked lakes increased REDOX potential at the sediment-water interface (Table 2.4). Oxidation potential (E_{hf}) at the interface was as much as four times

greater for cores treated with O₂ or FeCl₃ relative to N₂ and D.E. reference cores (Fisher's LSD, $P < 0.001$, Figure 2.2a). In contrast, REDOX potential at the interface of the N₂ and D.E. reference cores and cores treated with lime, alum, lime+alum were indistinguishable (Fisher's LSD, Figure 2.2b). The REDOX response amongst cores collected from each of the three lakes did not differ (ANCOVA, Table 2.4) and so the data were pooled by treatment. Treatments with O₂, FeCl₃, or a combination of both raised Eh_f at the sediment-water interface in cores from all three lakes.

Both REDOX sensitive and insensitive chemical treatments decreased P concentrations (TP_f, SRP_f) in the overlying water when compared to the N₂ and D.E. reference cores (Table 2.4; Figures 2.3 a & b). With the exception of O₂ and lime, TP_f and SRP_f concentrations were lowered equally by all treatments relative to the reference (Figures 2.3 a & b). Lime treatments decreased TP_f to 67% of pre-treatment concentrations, while O₂ maintained TP_f indistinguishable from TP_i. Neither lime nor O₂ treatments caused a detectable change in SRP_f in the sediment cores. The sediments from all three lakes treated with FeCl₃, and FeCl₃+O₂ became a net P sink: TP_f dropped to 14 and 11 % of TP_i and similarly, SRP_f decreased to 6 and 8% of SRP_i (Figure 2.3a). Treatments with alum and lime+alum decreased TP_f concentrations in the sediment cores to 26 and 28% of pre-treatment levels (Figure 2.3b), while SRP_f declined to 10 and 14% of SRP_i (Figure 2.3b). SRP ranged from two to eleven per cent of TP in both initial and final treatment conditions, and the proportion was not altered by treatment. Additionally, total phosphorus RR calculated for cores treated with lime, FeCl₃, alum, FeCl₃+O₂, and lime+alum were all negative, indicating a net removal of TP from water overlying the sediment (Table 2.6). As was found for REDOX potential, cores from the three

lakes did not differ in TP and SRP concentrations (Table 2.4). However, there was a lake-treatment interaction (Table 2.4) for the TP response, which was explained by the large difference in baseline TP values between cores collected from Amisk and the two other lakes. TP_i and TP_f concentrations in cores from Amisk Lake were 25-50% of the concentrations in cores from Baptiste and Crooked lakes. The lower TP concentrations observed in cores from Amisk Lake were caused by oxidation of sediment by the O₂ treatments administered for the 5 years prior to this study (Prepas and Burke 1997).

DO concentrations were most variable in the cores treated with O₂, while pH varied greatest in the cores treated with FeCl₃. Except in cores treated with O₂ where DO concentrations were 6 to 7 times those of the reference cores, concentrations of DO in the overlying water were not different between chemically-treated and reference cores (ANOVA, Table 2.4). As DO responses were not detectably different between lakes, data were pooled for the three lakes (Table 2.5). Consistent concentrations of O₂ were difficult to maintain in the sediment cores during the experiments. DO concentrations in the oxygen-treated cores were associated with *SE* values of 0.8 to 1.1 mg•L⁻¹ (Table 2.5). pH also varied among treatments (ANCOVA, Table 2.4). Treatments with the FeCl₃ decreased pH in the cores to 52-57% of the pH measured in the N₂ reference cores. In cores receiving all other treatments the average pH in the cores was held within the range of pH found in these three lakes (Table 2.5). During the experiments, O₂ treatments raised DO concentrations in the water overlying the cores relative to the reference cores; while except in treatments with FeCl₃, pH was successfully held in the range usually found in these lakes.

Concentrations of TP and SRP, and total phosphorus RR (Table 2.6) were related to the REDOX characteristics at the interface for cores treated with O₂, FeCl₃, FeCl₃+O₂ or N₂ reference cores. Log TP_f concentrations increased when Eh_f and pH_f decreased (Table 2.7). In contrast, increases in the log SRP_f concentration and RR were only associated with decreases in Eh_f (Table 2.7). When the data from overlying water in the sediment cores were examined individually, there were no significant pH terms included in the regression equations. The pH term was an artifact of the iron treatments and was not related to log TP_f when iron data were excluded from the analysis ($\log \text{TP}_f = 2.784 - 0.001(\text{Eh}_f)$, $P < 0.05$, $r^2 = 0.25$). Additionally, when data were separated by lake, the r^2 of the relationships between Eh_f and RR were increased in cores from Amisk and Crooked lakes. Separation of the data also increased r^2 for the relationships of Eh_f with log TP_f in Amisk and Baptiste lakes, and with log SRP_f in Baptiste Lake (Table 2.7). Based on the regression analyses in Table 2.7, REDOX potential at the sediment-water interface explains from 29 to 89% of the variability observed in P concentration in the overlying water.

Sediment geochemical characteristics were tested for a relationship with TP release rates from the cores. Mean sediment concentrations of iron (Fe_s), calcium (Ca_s) and sodium hydroxide extractable-P (NaOH-P), as well as the ratio of iron to phosphorus (Fe_s/TP), calcium to phosphorus (Ca_s/TP), and water composition (%) of the sediments are given in Table 2.8. With the exception of TP in sediment, sediment geochemistry measures that are associated with binding of P in the sediment (Fe_s, Fe_s/TP, Ca_s and Ca_s/TP ratios) were not related to total phosphorus RR in the cores. However, log TP in sediment was positively related to log RR for cores from all three lakes ($\log \text{RR} = 0.58 + 1.47(\log \text{TP})$ Eq. 1, Figure 2.4, $r^2 = 0.33$, $P < 0.01$).

Table 2.3: Correlation coefficient (r) between TP and pH, dissolved oxygen (DO), nitrite + nitrate ($\text{NO}_2^- + \text{NO}_3^-$), ammonium (NH_4^+), sulfate (SO_4^{2-}), or calcium (Ca^{2+}), in the water immediately overlying (1 m) the bottom sediment in Amisk, Baptiste and Crooked lakes. Data are presented from the summer of 1993 for all three lakes, and DO in Amisk Lake for 1980-85, prior to treatment with O_2 (Prepas and Burke 1997, Reedyk et al. in press). Sample sizes (n) are given in parentheses.

<u>Parameter with TP</u> <u>REDOX Related</u>	<u>Amisk</u>	<u>Baptiste</u>	<u>Crooked</u>
DO (1993) (1980-1985)	-0.70**(18) -0.61* (10)	-0.61*(11)	-0.63*(11)
$\text{NO}_2^- + \text{NO}_3^-$	-0.86**(9)	-0.43 (6)	-0.83*(6)
NH_4^+	n a	n a	0.73*(7)
SO_4^{2-}	-0.45 (10)	-0.92**(9)	-0.94**(8)
<u>REDOX Unrelated</u>			
pH	-0.28 (9)	-0.87*(8)	-0.92*(9)
Ca^{2+}	0.51 (10)	0.33 (10)	0.78**(9)

* $P \leq 0.05$

** $P \leq 0.01$

na, not analyzed

Table 2.4: Probabilities associated with ANCOVA analyses of data from sediment cores collected from Amisk, Baptiste and Crooked lakes. Final REDOX potential (EH_f), total phosphorus (TP_f), soluble reactive phosphorus (SRP_f) and pH (pH_f) are the dependent variables with lake and treatments as factors (covariates are initial measures of Eh, TP, SRP and pH respectively). Differences in dissolved oxygen (DO) and total phosphorus release rates (RR) among lakes and treatments were analyzed by ANOVA as initial DO concentrations and RR were not measured.

Independent Variables:	Lake	Treatment	Lake•Treatment Interaction	Covariate (Initial Conditions)
Dependent Variables (n)				
Eh _f (80)	0.19	**	0.46	0.84
TP _f (80)	0.06	**	*	0.09
SRP _f (74)	0.19	**	0.07	0.97
DO (80)	0.13	*	0.08	na
RR (80)	0.35	*	0.11	na
pH _f (80)	0.45	*	0.68	0.53

* $P < 0.01$

** $P < 0.001$

na, not analyzed

Table 2.5: Mean ($\pm SE$) Dissolved Oxygen (DO) concentrations and final pH (pH_f) for each treatment and reference condition in the water overlying the sediment in the cores. For each parameter means sharing the same letter are not different ($P > 0.01$, Fishers LSD *post hoc* test). Data were pooled for Amisk, Baptiste and Crooked lakes for $n=3$ for each treatment.

<u>Treatment</u>	<u>Mean DO</u> <u>mg • L⁻¹</u>	<u>Mean pH_f</u>
<u>Reference</u>		
Nitrogen (N ₂)	0.40 ± 0.20 ^a	7.1 ± 0.1 ^a
Diatomaceous Earth (D.E.)	0.33 ± 0.06 ^a	7.7 ± 0.1 ^a
<u>Experiment</u>		
Oxygen (O ₂)	2.47 ± 0.79 ^b	7.5 ± 0.1 ^a
Iron III Chloride (FeCl ₃)	0.03 ± 0.02 ^a	4.0 ± 0.5 ^b
FeCl ₃ & O ₂	3.06 ± 1.10 ^b	4.4 ± 0.6 ^b
Alum	0.13 ± 0.04 ^a	7.4 ± 0.2 ^a
Lime	0.18 ± 0.05 ^a	8.9 ± 0.3 ^a
Lime & Alum	0.30 ± 0.07 ^a	8.1 ± 0.2 ^a

Table 2.6: Total phosphorus release rates (RR) calculated from post-treatment total phosphorus concentrations for the sediment cores collected from Amisk, Baptiste and Crooked lakes. Data are pooled for the three lakes and for both trials resulting in $n=3$ per treatment.

<u>Treatment</u> <u>Reference</u>	<u>Mean RR ($\pm SE$)</u> $\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$
Nitrogen (N ₂)	7.3 \pm 4.0*
Diatomaceous Earth (D.E.)	5.7 \pm 2.5*
<u>Experimental</u>	
Oxygen (O ₂)	1.9 \pm 1.0
Lime	-0.9 \pm 0.5
Iron III Chloride (FeCl ₃)	-1.5 \pm 0.6*
Alum	-1.6 \pm 0.2*
Lime+Alum	-2.1 \pm 0.5*
Iron III Chloride + Oxygen (FeCl ₃ +O ₂)	-2.3 \pm 0.3*

* mean is different from 0 ($P<0.05$)

Table 2.7: Step-wise regression equations relating total phosphorus release rate (RR), final soluble reactive phosphorus concentrations (SRP_f) and final total phosphorus concentrations (TP_f) to final REDOX potential corrected to pH 7 (E_{hf}), final pH, or both in sediment cores collected from Amisk, Baptiste and Crooked lakes. Only data collected from the water overlying the sediment cores treated with oxygen (O₂), iron III chloride (FeCl₃), the combination of O₂ and FeCl₃, and the nitrogen (N₂) reference cores were used in the models. TP and SRP were log₁₀ transformed to meet assumptions of linear regression.

Lakes	Equation	<i>n</i>	<i>r</i> ²	<i>P</i>
<u>All</u>				
RR	3.19 - 0.01(E _{hf})	40	0.29	< 0.01
log SRP _f	0.667 - 0.002(E _{hf})	40	0.47	<<0.001
log TP _f	3.04 - 0.118(pH7) - 0.002(E _{hf})	40	0.57	<<0.001
<u>Amisk</u>				
RR	2.707 - 0.008(E _{hf})	8	0.89	<0.001
log SRP _f	1.197 - 0.002(E _{hf})	8	0.48	0.05
log TP _f	2.324 - 0.002(E _{hf})	8	0.83	<0.01
<u>Baptiste</u>				
RR	4.91 - 0.01(E _{hf})	16	0.20	0.08
log SRP _f	0.739 - 0.002(E _{hf})	16	0.76	<<0.001
log TP _f	2.433 - 0.001(E _{hf})	16	0.62	<<0.001
<u>Crooked</u>				
RR	3.206 - 0.01(E _{hf})	16	0.49	<0.01
log SRP _f	0.733 - 0.001(E _{hf})	16	0.30	<0.05
log TP _f	2.423 - 0.001(E _{hf})	16	0.49	<0.01

Table 2.8: Characteristics of surficial sediments (0-4 cm) from nitrogen treated reference cores from Amisk, Baptiste and Crooked lakes, Alberta. These data include surficial sediments from two additional cores collected at the same time from Baptiste Lake. Total phosphorus (TP), total iron (Fe_s), Fe_s/TP ratio, total calcium ($\text{mg}\cdot\text{g}^{-1}$)/TP ratio(Ca_s/TP) ratio, NaOH extractable phosphorus (NaOH-P) and water content (%) values are reported as mean $\pm SE$ for cores from each lake.

<u>Lake</u>	TP $\text{mg}\cdot\text{g}^{-1}$	Fe_s $\text{mg}\cdot\text{g}^{-1}$	Fe_s/TP	Ca_s/TP	NaOH-P $\mu\text{g}\cdot\text{g}^{-1}$	Water Content (%)
Amisk	1.5 ± 0.1	17.7 ± 7.5	12.3 ± 3.2	38 ± 8.1	31.9 ± 4.7	97.4 ± 2.2
Baptiste	3.3 ± 0.7	27.6 ± 4.8	8.7 ± 1.8	17 ± 3.3	96.8 ± 22.1	96.0 ± 1.2
Crooked	1.6 ± 0.1	25.2 ± 3.1	16.0 ± 5.3	31 ± 7.4	61.0 ± 4.2	96.2 ± 2.2

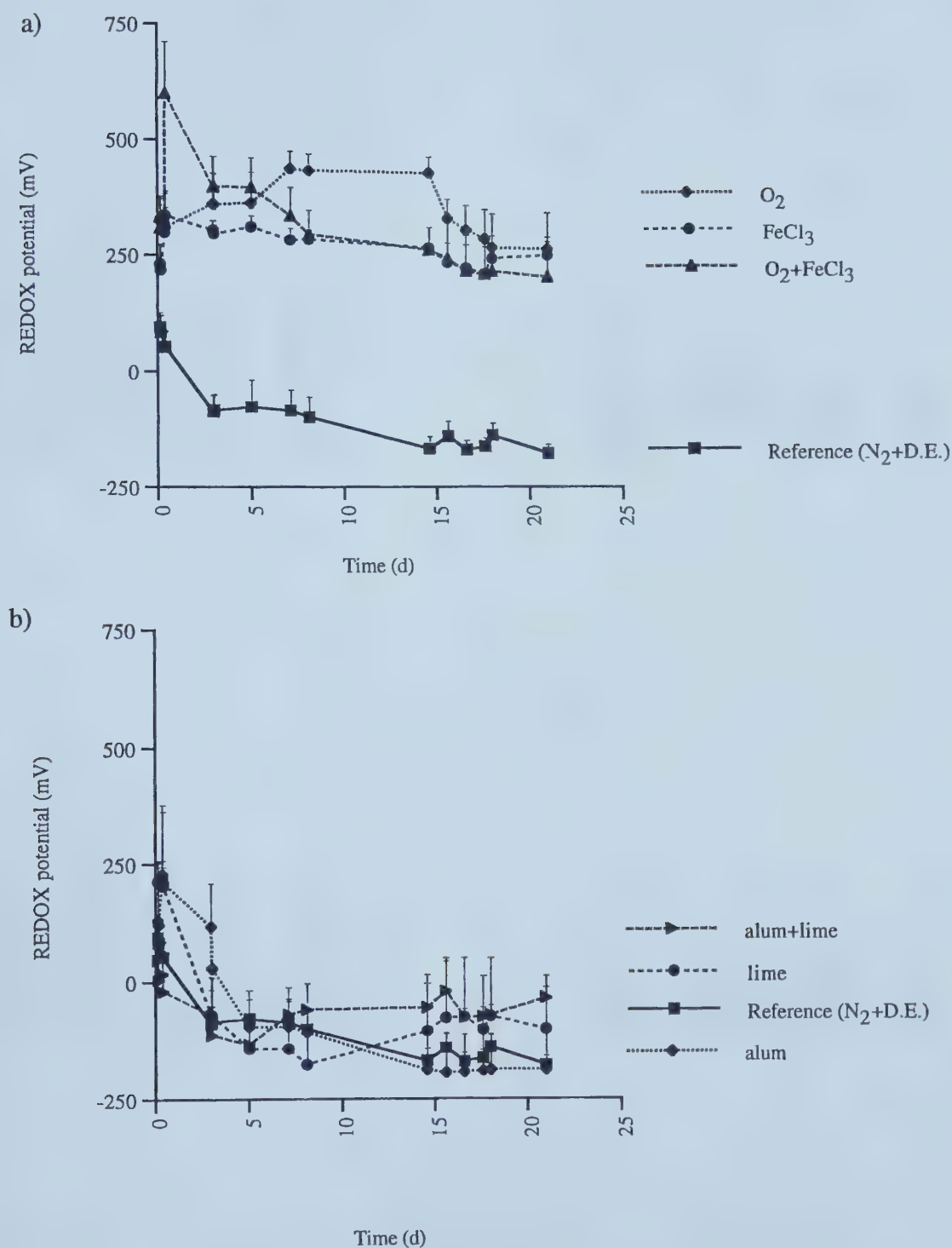


Figure 2.2: REDOX potential (mean \pm SE) at the sediment-water interface in the cores treated with: a) oxygen O_2 , $FeCl_3$ or $FeCl_3+O_2$; b) alum, lime, lime+alum and compared to reference cores. Data were pooled for Amisk, Baptiste and Crooked lakes for both trials such that $n=3$ per treatment condition

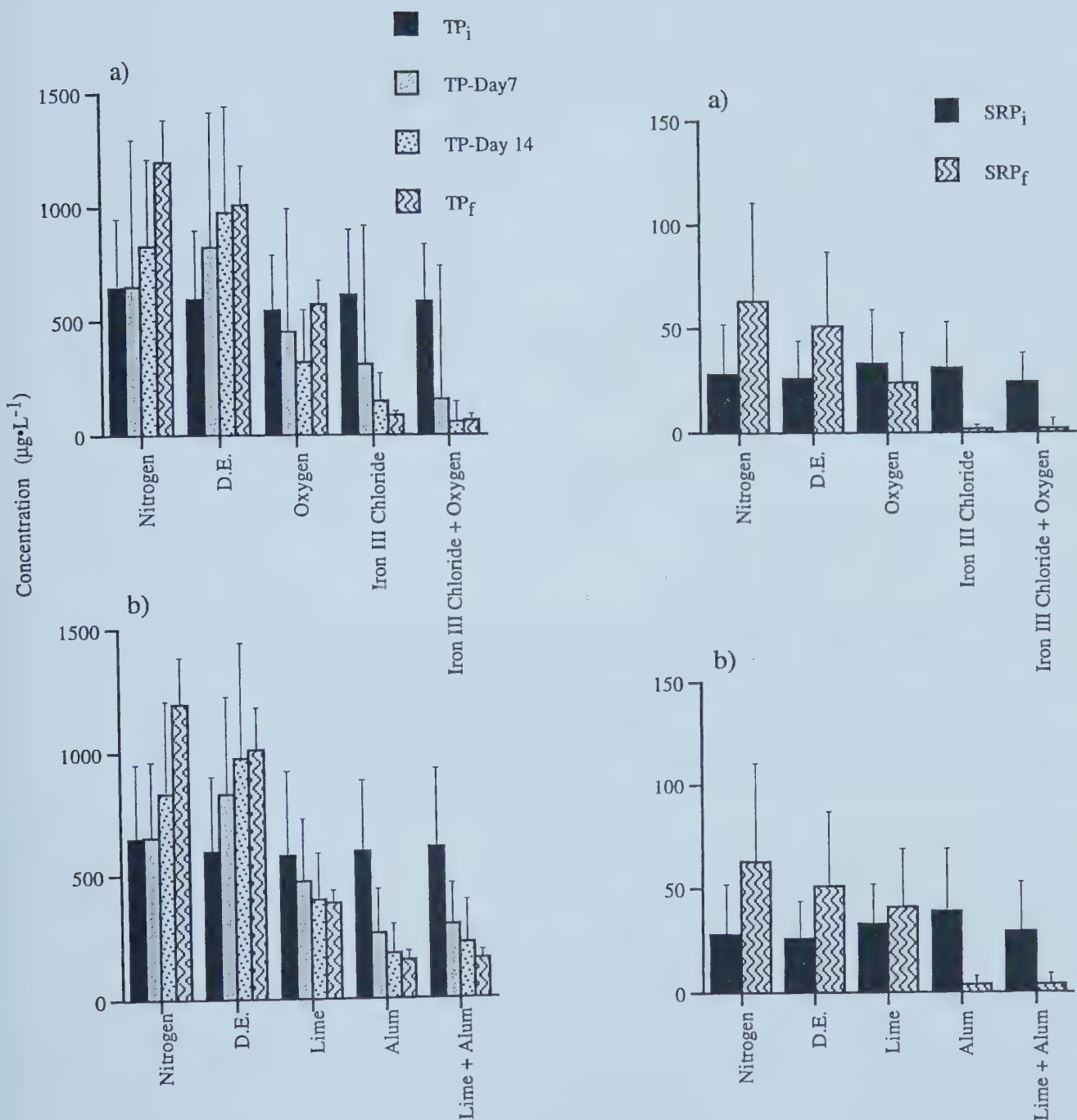


Figure 2.3: Mean ($\pm SE$) total phosphorus (TP) and soluble reactive phosphorus (SRP) concentrations pre-treatment (TP_i and SRP_i), post-treatment (TP_f and SRP_f) and, in the case of TP, on days 7 ($\text{TP}_{\text{Day 7}}$) and 14 ($\text{TP}_{\text{Day 14}}$). Cores were treated with: (a) O_2 , FeCl_3 or $\text{FeCl}_3 + \text{O}_2$, or (b) lime, alum or lime+alum and compared to references cores bubbled with N_2 gas with and without a diatomaceous earth (D.E.) flocculant. Data were pooled for Amisk, Baptiste and Crooked lakes across trials with $n = 3$ per treatment.

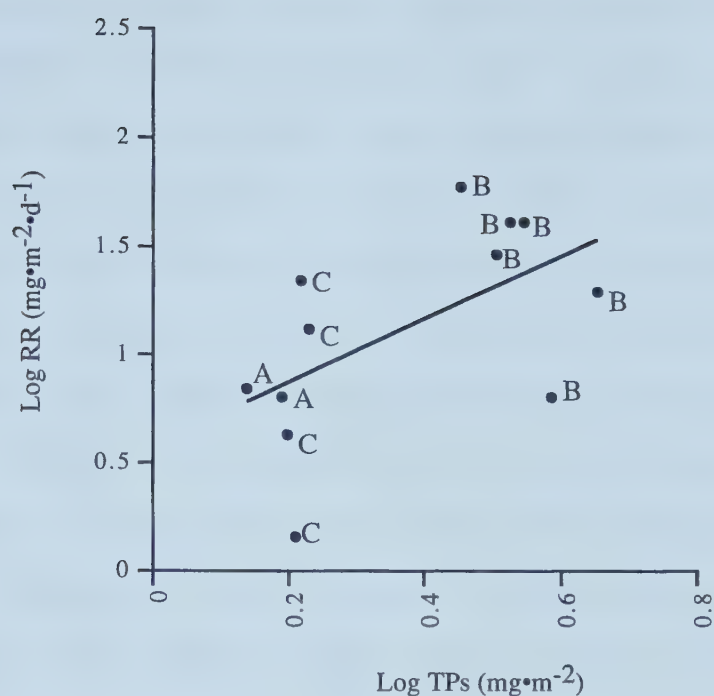


Figure 2.4: Linear regression of TP release rate (RR) versus total phosphorus concentration in sediment (TP_s) in the nitrogen treated reference cores from Amisk (A), Baptiste (B) and Crooked (C) lakes ($\log RR = 0.58 + 1.47(\log TP)$; $r^2=0.33$, $P<0.01$, $n = 12$). Sediment data from two additional cores collected from Baptiste Lake at the same time are also included in the analyses.

2.4: Discussion

Contrary to expectations, REDOX treatments were not detectably more effective than REDOX insensitive treatments in decreasing TP_f in sediment cores collected from three lakes on the Boreal Plain. Oxygen treatments did not decrease TP_f. In contrast the treatments with lime, alum, lime+alum, FeCl₃, and FeCl₃+O₂ decreased TP_f compared to pre-treatment levels. The effect of lime in the sediment cores was consistent with *in situ* observations from a similar single dose treatment on a lake in this geographic region (Reedyk et al. in press). The O₂ treatments in the sediment cores were less effective than treatments delivered *in situ* to Amisk Lake, where mean June-August hypolimnetic TP concentrations were decreased by 54% during treatment (Prepas and Burke 1997). During the experiments concentrations of DO in the cores were variable and only reached 53 to 67% of the mean June-August hypolimnetic DO concentrations achieved by Prepas and Burke (1997) during the treatment of Amisk Lake (Table 2.5). With the exception of lime and O₂, SRP_f concentrations were decreased by a similar amount as TP_f for each treatment. The percentage of TP accounted for by SRP remained constant for all treatments which indicated that some other component of TP was being removed by treatment from the water column. Total dissolved phosphorus was most likely being removed by the treatments, as D.E. reference treatments would have caused the same effects as flocculant treatments on particulate P.

REDOX Sensitive Treatments

Aeration with O₂ did not decrease SRP_f or TP_f concentrations in the cores (Figures 2.3a). These lake sediments may have failed to respond well to O₂ treatment because biochemically available iron concentrations were low (Prepas 1990a, Manning et al. 1994, in press, Murray 1995). It is likely that

sediment binding capacity for P is maximized under oxic conditions and it is only possible to improve P retention in sediment with the addition of Fe (Jaeger 1994). There were larger decreases in TP_f and SRP_f concentrations with treatments of $FeCl_3$ alone and in combination with O_2 .

Treatments with $FeCl_3$ lowered pH in water overlying the sediments in cores (Tables 2.4 & 2.5). A similar lowering of pH was not observed *in situ* by Böers et al. (1994), and is likely an artifact of low water volume in the experimental cores relative to the water volume overlying sediments in lakes. The impact of $FeCl_3$ treatments on pH_f explains the inclusion of a pH term in the regression predicting log TP_f concentrations from Eh_f (Table 2.7). In addition to raising Eh_f at the interface, $FeCl_3$ treatments provide adsorption sites for P as $Fe_x(OH)_n$ species form in the water column (Morel 1983). The formation of the iron hydroxide species explains the lowered pH_f in the sediment cores. The low pH likely contributed to increased P sorption by the sediment as iron tends to stay oxidized under conditions of low pH (Lijklema 1976, Morel 1983). At low pH, the solubility controlling solids are predominantly polymeric hydroxo species (Morel 1983), such as $Fe_3(OH)_4^{5+}$, $Fe_2(OH)_2^{4+}$, $FeOH^{2+}$ and $Fe(OH)_2^+$ (Morel 1983), capable of complexation with available phosphate (Lijklema 1976). Additionally, iron III ions may also be acting as electron acceptors for bacteria and thus may be mediating bacterial P release. Over the 3 weeks of this study, chemical precipitation most likely explains the impact on P concentrations of $FeCl_3$ and $FeCl_3+O_2$ treatments.

While in the short term, the $FeCl_3$ and $FeCl_3+O_2$ treatments decreased P release from the sediments equally when compared to alum, with and without lime, the long-term effectiveness of iron treatments *in situ* for these lakes is

questionable. Given the strong reducing environment of the sediment-water interface, it seems reasonable that in short periods of time, iron added would be reduced to pyrite and thus become unavailable to bind P as concluded by Manning et al. (1994, in press) based on sediment biogeochemistry in both Amisk and Baptiste lakes. Similarly, Quaak et al. (1993) also found that the long-term effectiveness of FeCl_3 treatments *in situ* was questionable, although short-term decreases in P loading from sediments were dramatic. Aeration, in combination with iron, might prolong the effectiveness of these treatments. However, aeration would necessarily have to be continuous throughout both summer, and ice cover in winter to prevent formation of pyrite. Aeration can improve the habitat for fish and other species in addition to lowering P concentrations (Prepas et al. 1997a), which may be a contributing factor in the decision to employ aeration treatments with or without FeCl_3 .

REDOX Insensitive Treatments

Treatment with lime and/or alum decreased TP_f concentration in the water column of the cores. Lime did not change SRP_f , while SRP_f concentrations were decreased by alum and lime+alum treatments by the same relative amount as TP_f . The relative effectiveness of lime treatments in the cores was consistent with *in situ* data from a single dose treatment applied by Reedyk et al. (in press) to a lake in the Boreal Plain. TP_f concentration changes in cores from Baptiste and Crooked lakes were more variable in response to lime than were those from Amisk Lake. There were inverse relationships between pH and hypolimnetic TP concentrations *in situ* from both Baptiste and Crooked lakes, while a positive correlation between Ca^{2+} and hypolimnetic TP concentration was also observed *in situ* in Crooked Lake (Table 2.3). In sediments from all three lakes the Ca_s/TP ratio is double that of Fe_s/TP (Table

2.8). These data support classifying the sediments as Type III, where apatite solubility controls release of P from sediments (Driscoll et al. 1993, Danen-Louwerse et al. 1995). Driscoll et al.'s (1993) model of Ca^{2+} as the controlling ion for P release may explain the effectiveness of lime application in decreasing TP_f in the cores from the three lakes. Calcite precipitation as the controlling solid phase is consistent with *in situ* data from lakes treated with lime (Prepas et al. 1997b, Reedyk et al. in press) and with data from Gonsiorczyk et al. (1998) in a hardwater eutrophic lake in the Baltic region of Germany. It appears likely that apatite solubility is the controlling solid in the precipitation of P in these lakes, which is consistent with Type III sediments but inconsistent with the REDOX sensitivity observed both in the cores and *in situ*.

SRP_f and TP_f concentrations decreased in cores from the three lakes relative to pre-treatment concentrations (TP_i and SRP_i), when treated with alum and lime+alum. The RR and P concentrations data indicate that sediments are acting as net P sinks (Figure 2.4 b). These flocculating agents act as additional adsorption sites for P in the superficial sediments, increasing P retention by the sediments (e.g. Cooke 1993). The pH changes that are often associated with lime and alum treatments (Cooke 1993) were not observed in this study because of the high buffering capacity of the water column and sediments. Cores treated with alum, lime and lime+alum had mean pH_f (Table 2.5) close to the seasonal ranges measured in water columns of these lakes in previous work: Amisk 8.7-8.9, Baptiste 7.8-8.8 (Prepas 1990a, Prepas 1990b), and Crooked 8.3-8.5 (Reedyk et al. in press).

REDOX Sensitivity of P Release

TP and SRP concentrations and total phosphorus RR in the cores were related to increases in E_{hf} at the interface (Table 2.7). These relationships are consistent with Mortimer's model (1941, 1942), where REDOX potential below 100 mV at the sediment-water interface explains increases in phosphorus concentration in water overlying bottom sediment in lakes. The relationships between REDOX potential and measures of P concentration in the cores were consistent with the correlations in water chemistry observed in the hypolimnion of the three lakes during summer 1993 (Tables 2.7 & 2.3). According to the Einsele and Mortimer models, the relationship between P release and REDOX potential should be based upon iron dynamics at the interface (Mortimer 1941, 1942, 1971, Lijklema 1976). The total iron to total phosphorus ratio in sediments (Fe/TP) should equal or exceed 10 if iron is regulating P release (e.g., Caraco et al. 1993). Except for sediments from Baptiste Lake, Fe_s/TP ratios in the sediments analyzed did exceed 10 (Table 2.8). However, the Fe_s/TP ratios were not related to P levels in the water overlying the cores from the three lakes, suggesting that factors other than iron dynamics must be regulating P release.

The REDOX sensitivity of the three lake sediments would designate them as Type II sediments according to Boström and Pettersson's model (1982). Type II sediments are assumed to be REDOX sensitive with P release regulated by adsorption and coprecipitation on iron and aluminum hydroxides and oxides (Boström and Pettersson 1982). However, sediment P analysis conducted in this study indicated that less than 5% of TP in sediment is NaOH-P, (Table 2.8) and these values are consistent with data from previous studies (Manning et al. 1994, in press, Prepas unpublished). Small NAI-P fractions in the sediments

are also consistent with the predominance of montmorillonite clay in the region, characteristic of lacustrine strata (Canadian Soil Survey 1978). The clays are low in iron and aluminum, have a net negative charge (Bohn et al. 1985), and except when P precipitates with calcium, are unlikely to bind or sorb large amounts of the phosphate anion (Bohn et al. 1985). Given the low NAI-P fraction in the Alberta lake sediments, it is unlikely that iron dynamics explain the kinetics of P release/sorption from these sediments.

Sediments designated as Type II by Boström and Pettersson (1982) had much higher NAI-P fractions, as high as 20% of sediment P. Not only are the NAI-P fractions in the sediments from these Alberta lakes less than those of Boström and Pettersson (1982), but available iron concentrations in the water column of these lakes are also low (Prepas 1990a, Prepas 1990b). The major iron fraction in the sediments of Amisk and Baptiste lakes is pyrite (Manning et al. 1994, in press). The low fraction of sediment P found as NAI-P is likely a result of the predominance of the mineral pyrite in sediments of Amisk and Baptiste lakes (Manning et al. 1994, in press).

In data sets from 51 lakes, Caraco et al. (1993) found that the Fe_s/P ratio was most likely controlled by sulfate REDOX cycles rather than the classical iron cycle suggested by earlier studies (e.g., Mortimer 1941, 1942, 1971). In the Caraco et al. (1993) model, little P is bound by iron under reducing conditions as pyrite is known to provide fewer sorption sites for P (Murray 1995). Iron sulfide precipitation in these lakes is supported by predominance of pyrite in the bottom sediment of Baptiste and Amisk lakes (Manning et al. 1994, in press). Additionally, sulfate and TP concentrations were negatively correlated in the hypolimnetic water over the bottom sediments of Crooked and Baptiste

lakes (Table 2.3). The mean potential at the sediment-water interface of the N₂ reference cores in this study was -158 mV (corrected to the standard hydrogen electrode potential), which is in the range of potentials at which sulfate reduction and methane production occurs (Stumm and Morgan 1981). Methane concentration in water overlying the cores from Baptiste Lake was in the range of 1700-3000 ppm (K. Burley, J. Chanton (Florida State U., FLA) and G. Whiting (Christopher Newport U., VA) unpublished). Therefore, methane and sulfate REDOX cycles likely control the iron cycles of these lakes and thus, REDOX dependent P release (Caraco et al. 1989, 1993). Regulation of P release by methane and sulfate REDOX cycles is consistent with microbial-mediated P exchange across the interface and, based on the regression with Eh_f (Table 2.7), may explain as much as 29-89% of P release from sediments in the cores from these three lakes. The life cycle of the *Acinobacter spp.* bacteria alternates between periods of P release during anoxic conditions and P storage during oxic conditions (Davalaaar 1993), which is consistent with conditions *in situ* (Prepas and Burke 1997, Reedyk et al. in press) and in the cores.

Of all the sediment chemical parameters measured (Table 2.8), only log TP in sediment was related to log RR in the water overlying the sediment. This relationship is consistent with a similar relationship described by Nürnberg (1988), however, unlike Nürnberg, RR and TP in bottom sediment were not related. The slope and intercept of Nurnberg's regression fell within one *SE* interval of the slope and intercept of the regression from the sediment cores from Amisk, Baptiste and Crooked lakes. The differences in the actual values of the coefficients were likely a result of the smaller sample size in this study compared to Nürnberg's (Alberta lakes $\log RR = 0.58 + 1.47\log(TP)$; Nurnberg: $\log RR = 0.80 + 0.76\log(TP)$). The RR predicted for the three lakes by

Nürnberg's log RR versus log TP in sediment regression (Amisk 8.4 ± 0.5 , Baptiste 12.1 ± 5.3 , Crooked $8.1 \pm 1.6 \text{ mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$) were consistent with the RR observed *in situ* (Amisk 6.2, Baptiste 11, Crooked $4.25 \text{ mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, Prepas 1990a, 1990b, Reedyk et al. in press). RR measured in these cores were lower than the RR observed *in situ*, a pattern which is consistent with observations by Riley and Prepas (1984) in cores from two similar lakes in the same geographic region. Shaw and Prepas (1990) found a similar relationship between sediment SRP release and P content of sediment in cores from nine lakes from this region, including Baptiste Lake. P release was positively related to TP in sediment in these experimental cores, which is consistent with patterns observed in lakes from this region (Shaw and Prepas 1990), and from other North American lakes (Nürnberg 1988).

REDOX sensitivity of the sediments and the absence of a large NAI-P fraction is consistent with microbial release of P from organic storage. The relationship between log RR versus log TP in sediment is also compatible with bacterial mobilization, as sediment TP represents the pool of P available to bacteria for metabolism. Ca_s and Ca_s/TP ratios in the sediments of the cores were apparently unrelated to P release from sediment. However the negative correlation between pH and TP concentrations in the hypolimnion of Baptiste and Crooked lakes during the summer of 1993 suggest that apatite solubility is a controlling factor in P release from sediments in those two lakes. Apatite dissolves at low pH and would release P to the water column under conditions of low pH. The positive correlation between Ca^{2+} and TP in the hypolimnion of Crooked Lake is also consistent with apatite solubility regulating P release. Thus, the designation of these sediments as Type II or III is unclear. It is clear that the sediment-water interface, as modeled in the experimental cores, was a

highly heterogeneous environment with multiple factors influencing P release. Apatite solubility, and bacterial P storage/release in response to REDOX potential changes at the sediment-water interface conforms to findings in a hardwater eutrophic lake in the Baltic Lake district (Gonsiorczyk et al. 1998).

General Conclusions

Both the core experiments and *in situ* hypolimnetic data from summer of 1993 for the three study lakes suggest that the REDOX sensitivity of the sediments is bacterial mediated. These observations are consistent with the findings of Gonsiorczyk et al. (1998), and with the observations during the aeration of Amisk Lake with O₂ (Prepas and Burke 1997). REDOX potential and pH are useful variables in monitoring the conditions at the sediment-water interface that are associated with P release. While P release in cores from the three study lakes was REDOX sensitive, iron was likely not the P binding mechanism, as proposed by Boström and Pettersson for Type II sediments (1982). Based on the r^2 obtained for regressions of P concentrations with REDOX potential in this study, bacterial mediated P release may contribute as much as 29%-89% of internal P loading, and accounts for the REDOX sensitivity of P release observed in the laboratory experiments and *in situ*.

Treatments added to sediment cores from the three lakes were effective to different extents in decreasing P in the overlying water (O₂ and lime < alum or lime+alum or FeCl₃ or FeCl₃+O₂). Although alum is highly effective in regulating P concentration and P release from sediment, concerns about aluminum toxicity in lakes and cost may restrict the use of alum (Böers et al 1994). Cost and ease of administering the treatments are also factors that may

limit the use of treatments with FeCl_3 and O_2 . However, treatments to control internal P loading were effective in the cores and support chemical inactivation of P release as an effective tool. Treatments with oxidizing agents (e.g., O_2 , FeCl_3) may be universally effective in hardwater eutrophic lakes due to their impact on bacterial metabolism, as well as the addition of coprecipitation and adsorption sites, but may be limited in the duration of their effect by the REDOX conditions at the interface. Lime treatments are effective in decreasing TP and are considered to be environmentally more benign and potentially less expensive by many lake managers. However, multiple doses may be required to achieve long term decreases in TP, and pH must be carefully controlled (Prepas et al. 1997b). Selection of the specific treatment regime should take into consideration sediment chemistry of the lake, specifically iron chemistry and calcium chemistry. Testing treatments on sediment cores may be a cost effective means to select appropriate chemical treatments when few data exist for the lake and intensive sampling is not available.

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3.0: General Discussion

In situ data from the summer of 1993 suggest that sediments from the three lakes should have fit the Type II model (Boström and Pettersson 1982). That is, because of the correlation between total phosphorus concentrations in the hypolimnion (TP) and REDOX sensitive chemical species (Table 2.3), the sediments should have been REDOX sensitive and NAI-P should be the primary binding mechanism for phosphorus (P). Moreover, in the experimental cores, REDOX potential at the sediment-water interface (E_{hf}) was related to final total phosphorus concentration (TP_f), final soluble reactive phosphorus concentration (SRP_f) and total phosphorus release rate (RR) (Table 2.7). However, the mechanism proposed by Boström and Pettersson (1982), adsorption and coprecipitation from iron and aluminum, was not supported by the sediment chemistry data. A very small proportion of the total phosphorus in sediment (TP_s) was non-apatite phosphorus (NAI-P) (Amisk $2.1 \pm 0.2\%$; Baptiste $2.9 \pm 0.0\%$; Crooked $4.1 \pm 0.6\%$) and these values are consistent with other data from Amisk and Baptiste lakes (Manning et al. 1994, in press). These sediments were REDOX sensitive, yet the P release mechanism was not adsorption/desorption from iron and aluminum chemical species.

Sediment Geochemistry Models

Nürnberg's (1988) model predicted sediment P release in Canadian Shield lakes from total phosphorus in sediment (TP_s) with 21% of the P release explained by TP_s . Application of Nürnberg's (1988) regression equations to the study lakes predict the P release rates observed *in situ*. TP_s predicts sediment P release in these lakes, and log RR in the cores was also related to

TP_s (Figure 2.4), and, the relationship terms are not significantly different between the Alberta cores and those of Nürnberg (1988).

REDOX Sensitive Mechanisms

Amisk, Baptiste and Crooked lakes were low in iron, had low NAI-P fractions and yet P release was REDOX sensitive (Table 2.7). Few iron data exist for the water column of the three lakes and, unfortunately, I did not measure Fe in the water column of the cores. The existing iron data (Manning et al. 1994, in press) suggest that the mechanism may be explained by biological activity rather than chemical kinetics in these lakes. Sulfate reduction also occurs at the potentials measured in the cores from these lakes, indicating that P release and iron chemistry may be controlled by sulfate REDOX cycles linked to bacterial metabolism. There is also anecdotal evidence of active sulfate reduction in Baptiste and Crooked lakes as the deep water sediments from these lakes smell strongly of sulfides during sampling.

A number of authors have implicated bacteria in REDOX dependent regulation of P release at the sediment-water interface (Eckerrot and Pettersson 1993, Waara et al. 1993, Gächter and Meyer 1995, Gonsiorczyk et al. 1998). The results from the sediment core experiments and *in situ* data from the study lakes suggest that bacterial activity regulates from 29-89% of P release at the sediment-water interface in the study lakes. Studies have shown that bacteria, particularly *Acinobacter spp.*, are REDOX sensitive and are able to store P as polyphosphate (poly-P) under aerobic conditions and release P by metabolizing poly-P under anoxic conditions (Gächter and Meyer 1993). These bacteria are able to store P when oxygen, iron or nitrate are available for reduction, as well as when O₂ is available. The effectiveness of FeCl₃

treatments in the absence of oxygen corroborates this hypothesis, as the increased availability of Fe^{3+} for reduction would maintain P -storing conditions for *Acinobacter spp.* As potential drops below the level at which Fe^{3+} is reduced, the bacteria would metabolize their stored poly-P, and P is released as ortho-P. A reasonable test of this hypothesis would be to run core experiments over a longer period, comparing anoxic conditions with anoxic FeCl_3 treatments in sterilized and unsterilized cores. Thus, it would be possible to determine if unsterilized FeCl_3 treated cores begin releasing P again after Eh_f at the interface indicates the available Fe is reduced. This test would isolate the bacterial mechanism from a coprecipitation/adsorption mechanism associated with iron.

Insensitive Mechanisms

The effectiveness of lime treatments in decreasing P concentrations in cores from all lakes (Figure 2.3) suggests a role for apatite solubility in controlling P release from sediments. This pattern is consistent with the correlations between TP and pH observed *in situ* data from Baptiste and Crooked lakes, and the correlation between TP and Ca^{2+} in Crooked Lake (Table 2.3). Lime treatments should have been highly effective at the pH of the study lakes if apatite solubility is the controlling solid phase. Given the higher pH ranges in these lakes, the high calcium concentration, and the alkalinity of the water column and sediments, it was reasonable to find that lime would be effective. In cores from all three lakes, there were large variabilities associated with the TP_f and RR measures, therefore generalizations need to be conservative. It is reasonable to say that lime treatments were effective in limiting P in these lakes, which is consistent with results from other lakes in this region that have undergone treatment with lime (e.g. Murphy and Prepas 1990, Prepas et

al. 1997). While the lime treatments were not as effective as treatments with alum or FeCl_3 , they are considered by many lake managers to be more environmentally benign as long as pH impacts are controlled by dilution and dosage.

Alum treatments effectively decreased RR, TP_f , and SRP_f concentrations in cores from the three study lakes (Figure 2.3, Table 2.6). Alum is assumed to regulate P exchange at the sediment-water interface by adding aluminum oxides and hydroxides to the sediment. Thus, alum additions increase P-sorption capabilities of the sediment in the short term. Concerns surrounding the use of alum in lakes center on the toxicity of aluminum to biota (Cooke 1993). Aluminum should not dissolve from the sediment when pH is > 6.0 at the sediment-water interface (Cooke 1993). However if pH drops below 6.0 at the interface, then aluminum may dissolve and be released into the overlying water, where it would pose a serious risk to fish and other biota (Cooke 1993). Public concerns about aluminum toxicity for fish and humans often prevent its use as a treatment in lakes (Böers et al. 1994).

While conversion of particulate P to dissolved P is necessary for P flux from sediment it is also important to consider how the P is moving from the porewater into the overlying water (Boström et al. 1982). A variety of physical characteristics of the lake, such as fetch and mixing regimes, must be considered. Biota are also implicated through bioturbation (Boström et al. 1982). Models of P release to the overlying water column from bottom sediments must involve both dissolution and desorption mechanisms into porewater, and migration mechanisms from porewater to the overlying water. To manage P release from bottom sediment, it is possible to intervene at either

stage. Phosphorus release from cores receiving an inert floc treatment of diatomaceous earth (D.E.) was not significantly slowed. This suggests that simple diffusion is not the predominant mechanism for P migration from porewater. This observation supports the inference that flocculant treatments slow P release by both adsorption and precipitation, as a physical barrier (D.E.) alone shows little impact on P release.

Management Considerations

Since bacterial metabolism is the most likely REDOX mechanism controlling P release in these lakes, then treatments that inhibit the metabolic pathways that cause P release are reasonable solutions to internal loading of P.

Aeration, oxidizing agents such as Fe^{3+} , and nitrate additions to lakes may slow the bacterial metabolism and/or prevent P mobilization from bacteria (Foy 1986, Cooke 1993). Sediment treatments that enhance competition for electron donors/acceptors by species that do not mobilize P may also be a reasonable strategy. There may be limitations to the long-term usage of these treatments as the interface in these lakes frequently cycles through a strongly reducing phase (anoxic). Reduction of the available iron by sulfides may result in re-establishing a large exchangeable P pool. The addition of electron acceptors to the interface may also stimulate the growth of a larger bacterial population, which in turn leads to a faster metabolic processing of available oxygen and iron. Alternately, chemical inactivation of the sediment P and slight pH shifts at the interface may slow bacterial metabolism, and not alter the habitat for other benthic organisms that are critical to the food chain. Future work is necessary to demonstrate the role of bacteria in mobilization at the sediment-water interface before appropriate control strategies can be devised.

Currently, it is possible to use chemical treatment to slow the release of P from

bottom sediments. These treatments vary in their effectiveness, persistence and cost. However, this study demonstrates that FeCl_3 , O_2 , lime and alum alone or in combination, can decrease P release from bottom sediment.

Suggestions for Future Work

Future work on this question should center on reproducibility of these findings within the study lakes and in other lakes of similar chemistry and geological setting. An examination of the utility of electrodes for long-term monitoring in lakes and reservoirs is also an important extension of this project. Future core experiments and/or batch incubator experiments could categorize the bacteria present in the sediments and quantify their role in P mobilization from sediment. Additionally, tests of the long-term efficacy of sensitive treatments in lakes where seasonal anoxia leads to reducing environments, would also help in the selection of effective treatments for management of internal P loading.

General Conclusions

This study demonstrates a relationship between potential at the sediment-water interface and the release of P from bottom sediment in hardwater lakes. The effectiveness of lime treatments, as well as the lake chemistry patterns, implicate apatite as the solubility controlling solid regulating P release in these lakes. Patterns in lake chemistry from other studies (Prepas and Burke 1997, Reedyk et al. in press) suggest a bacterial role in P release that is consistent with the REDOX sensitivity observed despite the small proportion of sediment P associated with iron and aluminum. Any further work on sediment P release in these lakes should focus both on the role of bacteria at the sediment-water interface and apatite binding of P in sediment as mechanisms

to control P release. Apatite solubility coupled with bacterial metabolism as the two dominant mechanisms regulating P release is consistent with findings in another eutrophic hardwater lake in Germany (Gonsiorczyk et al. 1998).

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Waara T., Jansson M. and Pettersson K. (1993) Phosphorus composition and release in sediment bacteria of the genus *Pseudomonas* during aerobic and anaerobic conditions. *Hydrobiol.* **253**, 131-140.

Appendix A:

**A Test of the Reliability of Platinum REDOX Electrodes After 3
Weeks at Low Temperature and in Sediment**

Report previously submitted for partial fulfillment of requirements of Zoo 430.

Abstract:

This experiment tested the effects of storage at 10 °C and in sediment at 10 °C on platinum electrodes. The reliability of the electrodes was assessed by testing for differences in the measurement of the potential of a standard REDOX solution among three different storage conditions (room temperature, 10 °C, 10 °C in sediment). The measures of potential were submitted to an Analysis of Covariance using the Statgraphics[©] statistical package. No significant differences were found among the three groups of electrodes. The results of this study indicate that the reliability of platinum electrodes to measure oxidation/reduction potential during a three week period in sediment cores is not significantly affected by the sediment environment as has been previously been suggested by other authors.

Background:

Platinum electrodes have been used to measure reduction-oxidation (REDOX) potential in soils research (Walton-Day et al. 1990; Farrell et al. 1989; Sparks 1988; Pickering and Venemen 1984; Vepraskas and Bouma 1983; Bohn 1971) and aquatic literature (Jensen and Andersen 1992; Faulkner et al. 1985; Sholkovitz 1985; Hostettler 1984; Stumm and Morgan 1980; Mortimer 1971,1941,1942).

These measures are useful in predicting the chemical conditions in remote environments with little disruption to the system and in relating potential to the activity of microbes in these environments (Stumm and Morgan 1981).

There is a controversy over the accuracy of this measure of REDOX potential (Grundl and Macalady 1989; Stumm, Morgan and Hostettler 1985; Hostettler 1984; Faust and Aly 1981; Stumm and Morgan 1981; Fillos 1976; Bohn 1971; Whitfield 1969, 1974; Doyle 1968; Barnes and Back 1964; Baas Becking et al. 1960; Hayes et al. 1956; Mortimer 1941, 1942, 1971). The controversy centers upon issues surrounding the accuracy of the measure based upon the actual state of the electron and the precision of the measure over time (Stumm, Morgan and Hostettler 1985; Hostettler 1984; Stumm and Morgan 1981; Whitfield 1974; Bohn 1971; Mortimer 1971; Doyle 1968; Hayes et al. 1956). The issue of accuracy will not be addressed by this paper as the use of the electrodes as a qualitative descriptor of REDOX conditions is well accepted on all sides of the controversy (Stumm, Morgan and Hostettler 1985; Hostettler 1984; Stumm and Morgan 1981; Bohn 1971; Whitfield 1969, 1974; Mortimer 1971; Doyle 1968; Baas Becking et al. 1960; Hayes et al., 1956). The particulars of the debate center upon the strict interpretation of the electrode potential as a potential of a single REDOX couple (eg. $\text{Fe}^{2+} / \text{Fe}^{3+}$), (Grundl and Macalady 1989; Murphy and Lean 1975; Bohn 1971; Doyle 1968). The electrode potential is a mixed potential of all REDOX couples in solution and so in natural solutions it is a blended measure and not

readily interpreted as reflecting the state of one single REDOX couple (Stumm, Morgan and Hostettler 1985; Hostettler 1984; Stumm and Morgan 1981; Bohn 1971; Whitfield 1969, 1974; Mortimer 1971; Doyle 1968; Baas Becking et al. 1960; Hayes et al. 1956). In pure solutions of known composition it is possible to assign the measured potential to the single REDOX couple present in the solution (Grundl and Macalady 1989; Bohn 1971; Doyle 1968).

This experiment will test the stability of the electrodes after a period of three weeks in sediment cores from a hypereutrophic, sulfide rich lake. It will be possible to determine from the stability test whether the electrode performance degrades over time. Many authors suggest that over time, in either soils or sediments, the electrodes are progressively altered by the environmental conditions (Stumm, Morgan and Hostettler 1985; Hostettler 1984; Stumm and Morgan 1981; Bohn 1971; Whitfield 1969, 1974; Mortimer 1971; Doyle 1968; Baas Becking et al. 1960; Hayes et al. 1956). The degradation is supposed to be caused by an oxide coating deposited on the electrode which can only be removed by vigorous cleaning (Stumm, Morgan and Hostettler 1985; Hostettler 1984; Stumm and Morgan 1981; Bohn 1971; Whitfield 1969, 1974; Mortimer 1971; Doyle 1968; Baas Becking et al. 1960; Hayes et al. 1956). This study will examine the long term effects (3 weeks) of a temperature change to 10 °C and placement in sediments on the measurement the potential of a standard REDOX solution.

The REDOX potential of a standard REDOX solution of known potential (Light, 1972) will be measured with each electrode. The electrodes will be assigned one of three test conditions and will be left under these conditions for three weeks. At the end of the three weeks the electrodes will be removed from the

experimental conditions and the potential of the standard will again be measured. Differences among the groups will be tested by an Analysis of Covariance, and if significant differences are detected a Tukey's Test will be performed to determine homogenous groups (Zar 1984).

Problem:

Do platinum (Pt) REDOX electrodes accurately measure the REDOX potential of the surrounding environment after lengthy times *in situ*?

Hypothesis:

H₀: The measures of REDOX under each of the storage conditions does not change over time and thus there is no effect of sediment or temperature on the precision of the electrodes over time.

H_A: The electrode performance is impaired by placement in the sediment and/or temperature changes as reflected in significant differences of the precision of the measurement of a standard potential after time stored in sediment or temperatures of 10 °C.

Methods:

Thirty-six platinum (Pt) electrodes (Farrell et al. 1990) were used to measure the REDOX potential of a standard REDOX solution (Light 1972). The electrodes were placed in the standard solution and allowed to equilibrate for 1-h. The potential was read as electrical current in millivolts (mV) using a Beckman Θ 12 pH meter against a Ag/AgCl reference electrode with reference solution of 4M KCl. The readings were taken using the auto function to stabilize the fluctuations which occur with electrode readings. These thirty-six electrodes were randomly assigned to one of three experimental groups: group 1 which

were left to sit in sealed core tubes under room conditions; group 2 which were left to sit in sealed core tubes in an environmental chamber at 10 °C ; and group three which were inserted into sediment cores, sealed and then stored in an environmental chamber at 10 °C. All three groups were stored under the experimental conditions for three weeks. After this time period had elapsed, they were removed from their locations and again used to measure the REDOX potential of the same standard solution (Light, 1972). The same measurement protocol as the pretest measures was used. Prior to measuring the potential of the solution the electrodes were inspected for obvious signs of breaks or damage. Four electrodes were discarded due to apparent breaks in the electrode. The potential of the reference was not measured using the discarded electrodes and thus their values are excluded from the pretest measures as well.

Data were tested for normality graphically and by a Goodness of Fit Test, then analyzed for significant differences between groups in an Analysis of Covariance (ANCOVA), (Zar, 1984) where the pretest potential is the covariate.

Results and Discussion:

The electrode readings are presented grouped by experimental conditions in Table 1. The reading of the specific electrode before and after placement in one of the three experimental conditions is shown in column 2 and in column 3. Group 1 electrodes were stored at ambient conditions, group 2 electrodes at 10 °C and group 3 electrodes in sediment cores at 10 °C. There is a difference in potential of approximately 100 mV between the pretest conditions and the post-test conditions. This difference may have been caused by aging of the REDOX standard, aging of the reference electrode or a systematic aging of the

electrodes themselves under all conditions. Measurement of the potential of the same reference solution with bright, (cleaned), Pt electrodes yielded values in the same range as the electrodes from the experiment (472 mV +/- 25 mV). The evidence of this quick check of the system suggests aging of the reference solution is responsible for the observed drift.

The data were categorized and tested for normality prior to any analysis. The graphed cumulative proportions did not appear to be linear although a fitted regression line yielded an r^2 value of 0.924 for the pretest data and 0.934 for the posttest data. In order to better assess the normality of the data they were submitted to a Goodness of Fit Test (Zar, 1984). This test was selected as the number of observations was less than 150. The pretest data yielded a Chi Square value of 17.96 which was not significant at the 0.01 level (critical value for $\alpha=0.01, df=8$, is 20.090). The posttest data yielded a Chi Square value of 7.84 which was not significant at the 0.01 level (critical value for $\alpha=0.01, df=7$, is 18.475). The alpha level was selected at the 0.01 level as there are few measures and high natural variance occurs in any electrode measures. It would have been a better test had the mean and standard error measures for the standard solution been published with the techniques (Farrell et al. 1990; Light 1972). These values could be treated as population values in the normality test. Electrode measures commonly have reasonably high natural variance, in their readings and so a high alpha was used to reduce the chance of a Type I error. A Power Analysis was not performed to select sample size and to control for Type II error. Sample size was determined from the literature review in the context of what was logistically possible at the time.

After determining that the data could be assumed to be drawn from a normally distributed population, they were subjected to an Analysis of Covariance (ANCOVA) where the pretest measures were the covariate (Zar 1984). There were no significant differences in the three experimental groups ($F = 0.770$, $P > 0.05$) and the effect of the covariate, pretest values, was not statistically significant ($F = 0.013$, $P = 0.9126$). The results fail to support rejection of the null hypothesis. It has not been demonstrated in this experiment that electrodes are significantly altered in the ability to accurately measure a standard potential by either the temperature of the storage environment or by placement in sediment. These results suggest that Pt electrodes can be used in sediment cores for periods of up to 3 weeks without concern over the reliability and precision of the measure.

The covariate regression line does not explain a significant amount of the variation, $r^2 = 0.21$. The slope of the line is not significantly different from zero. These results indicate that variations in the electrodes do not account for much of the variation among the groups. If there were significant differences among the groups this result may have been of concern as variation between electrodes would be a reasonable explanation of this phenomenon. However, the lack of significance to the covariate as a source of variance among groups can be interpreted to indicate that the electrodes themselves are not significantly different either prior to storage in the different condition or after storage. Thus the electrodes are quite similar despite slight manufacturing differences.

This experiment could be improved by additional combinations of temperature and sediment conditions (types). It would have been valuable to monitor the

REDOX potential of the sediment profiles as an additional measure to determine if there were different sediment environments for the individual electrodes. It would also be of interest to determine if the presence or absence of water in the core tube would influence the outcome. The core tubes in question were not tested for oxygen concentration, which may also confound the environmental effects, as REDOX chemistry is affected by oxygen availability.

Extensions of this experiment should include a wider variety of conditions, longer duration to determine the point at which problems do occur, and a larger sample size. It is important to note that the four electrodes which were discarded due to breakage were from the sediment group and thus the mean for this group may be biased. In future designs it may be useful to include extra electrodes in the sediment groups as some breakage of the rather delicate (0.5-mm) wires is inevitable due to the coarseness of a sediment environment.

Conclusion:

The results of this experiment fail to show any effect of sediment or lowered temperature on the reliability of electrode measures of a standard potential over a three week period ($F = 0.770$, $P > 0.05$). The measures of potential were shown to be drawn from the normal population by a Goodness of Fit test (Zar 1984) (Chi Square values at $P > 0.01$).

Table 1: REDOX potential values for each electrode grouped by experimental conditions. Group 1 = ambient conditions, group 2 = 10 degrees C and group 3 = sediment cores at 10 degrees C.

Experimental Treatment	Pre-test Potential	Post-test Potential
1	570.5	471.1
1	570.6	450.9
1	571.7	472.6
1	562.9	472.3
1	574.1	476.0
1	584.0	473.3
1	577.8	470.3
1	576.3	473.9
1	561.1	468.2
1	564.3	472.0
1	566.1	473.4
1	560.2	468.5
2	576.7	469.0
2	578.0	469.2
2	575.8	460.2
2	574.9	472.4
2	553.9	470.8
2	542.0	461.0
2	556.3	463.0
2	550.1	462.0
2	547.0	486.6
2	575.4	472.6
2	573.8	471.4
2	549.8	471.1
3	574.8	464.6
3	573.7	456.2
3	563.1	459.0
3	560.8	470.0
3	539.5	492.1
3	564.5	490.8
3	553.8	410.5
3	548.8	456.8

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Appendix B:

Dissolved oxygen, pH, total phosphorus, soluble reactive phosphorus, and electrode potentials data for all cores from the three lakes

Table B-1: Final dissolved oxygen DO (mg•L⁻¹) data for the cores pooled for both trials for Baptiste and Crooked lakes, with single trial data from Amisk Lake.

Treatment	Lake	FINAL DO	Treatment <i>Mean</i>	<i>SE</i>
Nitrogen	Amisk	0.37		
		0.07		
	Crooked	0.31		
		0		
		2.12		
	Baptiste	0.22		
		0.42		
		0.13		
		0		
		0.39	0.4	0.2
Oxygen	Amisk	1.68		
		1.18		
	Crooked	0.83		
		8.63		
		2.1		
	Baptiste	1.27		
		1.24		
		1.09		
		5.86		
		0.83	2.5	0.8
Iron III Chloride	Amisk	0		
		0		
	Crooked	0.11		
		0		
		0		
	Baptiste	0		
		0		
		0.13		
		0		
		0.04	0.03	0.02
Iron III Chloride + Oxygen	Amisk	1.14		
		1.04		
	Crooked	6.65		
		9.73		
		0.33		
	Baptiste	0.87		
		1.35		
		8.39		
		0.04		
		1.03	3.1	1.1

Table B-1: Cont'd.

Diatomaceous Earth	Amisk	0.28		
		0.61		
	Crooked	0.17		
		0.26		
		0.26		
		0.35		
	Baptiste	0.44		
		0.24		
		0.04		
		0.68	0.3	0.1
Lime	Amisk	0		
		0		
	Crooked	0.2		
		0.31		
		0.2		
		0.57		
	Baptiste	0.03		
		0.26		
		0.2		
		0.07	0.2	0.1
Alum	Amisk	0.15		
		0.04		
	Crooked	0.17		
		0		
		0		
		0.22		
	Baptiste	0.39		
		0.04		
		0.07		
		0.2	0.1	0.04
Lime+ Alum	Amisk	0		
		0		
	Crooked	0.55		
		0.11		
		0.63		
		0.57		
	Baptiste	0.15		
		0.17		
		0.39		
		0.42	0.3	0.1

Table B-2: Initial (pH_i) and final (pH_f) pH data for all cores pooled for the three lakes from both trials with Baptiste and Crooked lakes and a single trial with Amisk Lake.

Treatment	Lake	pH _i	Mean pH _i	SE pH _i	pH _f	Mean pH _f	SE pH _f
Nitrogen	Amisk	7.40			7.40		
		7.35			7.30		
	Crooked	7.19			6.80		
		7.24			6.60		
		7.21			7.00		
	Baptiste	7.22			7.00		
		7.22			7.30		
		7.27			7.50		
		7.25			7.40		
		7.23	7.26	0.07	7.10	7.14	0.09
Oxygen	Amisk	7.60			7.40		
		7.37			7.50		
	Crooked	7.28			7.40		
		7.26			7.60		
		7.30			7.30		
	Baptiste	7.24			8.20		
		7.42			7.00		
		7.38			7.50		
		7.50			7.30		
		7.33	7.37	0.11	8.20	7.54	0.12
Iron III Chloride	Amisk	7.38			3.10		
		7.38			5.70		
	Crooked	7.20			2.40		
		7.25			2.50		
		7.23			3.80		
	Baptiste	7.23			5.10		
		7.25			2.40		
		7.30			5.50		
		7.30			3.40		
		7.27	7.28	0.06	6.00	3.99	0.46
Iron III Chloride + Oxygen	Amisk	7.35			6.30		
		7.33			5.70		
	Crooked	7.20			2.60		
		7.22			2.30		
		7.18			6.50		
	Baptiste	7.24			6.40		
		7.28			2.50		
		7.25			2.30		
		7.30			4.00		
		7.23	7.26	0.06	5.40	4.40	0.58

Table B-2: Cont'd.

Diatomaceous Earth	Amisk	7.42			7.70		
		7.36			8.20		
	Crooked	7.20			7.40		
		7.32			7.00		
		7.31			7.60		
	Baptiste	7.19			8.00		
		7.24			8.00		
		7.25			7.50		
		7.22			8.00		
		7.26	7.28	0.07	7.80	7.72	0.11
Alum	Amisk	7.58			7.10		
		7.35			8.10		
	Crooked	7.28			7.20		
		7.30			6.70		
		7.33			7.80		
	Baptiste	7.18			7.70		
		7.42			6.90		
		7.38			8.20		
		7.51			7.20		
		7.31	7.36	0.12	7.20	7.41	0.16
Lime	Amisk	7.38			8.80		
		7.38			8.10		
	Crooked	7.22			10.00		
		7.25			9.00		
		7.18			8.20		
	Baptiste	7.33			8.70		
		7.28			8.20		
		7.33			11.20		
		7.34			8.70		
		7.30	7.30	0.07	8.70	8.96	0.30
Lime+Alum	Amisk	7.33			8.30		
		7.31			8.50		
	Crooked	7.23			8.10		
		7.25			8.40		
		7.22			7.90		
	Baptiste	7.26			8.50		
		7.25			8.00		
		7.27			6.50		
		7.28			8.50		
		7.24	7.26	0.03	8.20	8.09	0.19

Table B-3: Total phosphorus (TP), including initial (TP_i) and final (TP_f) data for all the cores from the three lakes for both trials with Baptiste and Crooked lakes and a single trial with Amisk Lake.

Treatment	Lake	TP _i	TP Day 7	TP Day 14	TP _f μg•L ⁻¹	Treatment TP _f Mean	Treatment TP _f SE
Nitrogen	Amisk	166	227	445	567	1197	186
		170	282	495	604		
	Crooked	494	668	750	1038		
		557	576	563	552		
		1169	653	684	869		
	Baptiste	909	993	1097	1633		
		642	1153	1607	2147		
		611	861	1210	1351		
		845	869	1077	1180		
		900	214	348	2032		
Oxygen	Amisk	171	172	141	515	572	105
		121	160	194	177		
	Crooked	865	681	207	510		
		831	158	103	960		
		450	444	668	855		
		512	240	268	316		
	Baptiste	562	430	567	1121		
		595	1109	695	670		
		607	459	158	106		
		723	662	191	485		
Iron III Chloride	Amisk	143	73	59	30	87	19
		162	82	19	21		
	Crooked	958	365	91	19		
		967	339	39	126		
		559	415	345	199		
		434	331	297	146		
	Baptiste	757	195	182	133		
		591	1070	295	64		
		816	137	93	87		
		719	83	73	49		
Iron III Chloride + Oxygen	Amisk	204	87	3	28	65	27
		179	94	25	26		
	Crooked	805	293	14	24		
		1024	74	5	28		
		531	219	69	74		
		510	177	52	37		
	Baptiste	662	194	299	301		
		622	176	68	65		
		612	122	23	23		
		703	119	23	39		

Table B-3: Cont'd.

Diatomaceous Earth	Amisk	166	154	398	517		
		153	232	328	200		
	Crooked	879	963	1344	1392		
		847	819	1488	1626		
		421	934	1294	1534		
		459	725	1189	1271		
	Baptiste	602	924	1267	1305		
		596	1555	1398	1430		
		1114	1128	486	417		
		689	802	570	412	1010	174
Alum	Amisk	116	37	30	37		
		136	117	28	62		
	Crooked	990	589	214	101		
		931	277	253	211		
		504	309	296	192		
		528	168	84	83		
	Baptiste	647	257	292	335		
		598	529	342	346		
		728	99	193	154		
		728	231	78	39	156	36
Lime	Amisk	186	225	266	305		
		155	119	48	177		
	Crooked	626	505	623	590		
		1370	653	645	517		
		407	949	259	160		
		382	269	348	341		
	Baptiste	629	350	289	273		
		676	743	482	459		
		634	497	530	608		
		700	404	486	419	385	51
Lime + Alum	Amisk	123	67	34	42		
		116	76	35	39		
	Crooked	1131	505	623	181		
		766	449	193	126		
		519	480	297	293		
		452	354	208	216		
	Baptiste	777	347	289	226		
		546	102	272	330		
		734	346	200	101		
		893	215	68	46	160	33

Table B-4: Initial (SRP_i) and final (SRP_f) soluble reactive phosphorus data for cores from all three lakes pooled for both trials in Baptiste and Crooked lakes and a single trial in Amisk Lake.

Treatment	Lake	SRP _i μg•L ⁻¹	SRP _f μg•L ⁻¹	Mean ΔSRP	SE
Nitrogen	Amisk	22.6	99.5	34	11
		19.7	98.1		
	Crooked	12.2	11.2		
		11.4	28.1		
		4	1.9		
	Baptiste	6.2	12		
		56.6	123.6		
		59.3	99.2		
		63.4	89		
Oxygen	Amisk	18.9	16	-9	12
		12.5	77.1		
	Crooked	14.8	13		
		14	25.1		
		13.7	5.5		
	Baptiste	8.4	4.4		
		56.6	53.1		
		46.6	33.6		
		71.6	7.7		
		70.9	7.3		
Iron III Chloride	Amisk	23.4	4.8	-29	8
		17.8	0.4		
	Crooked	4.3	0		
		15.9	0.4		
	Baptiste	58.1	4.2		
		31.6	0		
Iron III Chloride + Oxygen	Amisk	63.8	0.8	-22	6
	Crooked	22.6	0.1		
		20	0		
		14	12.6		
	Baptiste	6.2	0		
		22.3	0.1		
		48.4	0.1		
		36.8	0		

Table B-4: Cont'd.

Diatomaceous Earth	Amisk	20	73.8		
		19.3	33.7		
	Crooked	9.9	12.3		
		14.4	15.2		
		4	119.4		
	Baptiste	6.2	49.6		
		40.2	81.7		
		47.7	81		
		36.5	19.2		
		56.3	24.3		
Alum	Amisk	20	4.4		
		20.8	1.5		
	Crooked	10.7	2.4		
		13.7	1.2		
		33.9	13.8		
	Baptise	4.3	0.4		
		75	5.7		
		68.6	7.1		
		79.8	0		
		66.4	3		
Lime	Amisk	21.5	42.4		
		21.1	32.6		
	Crooked	11.8	12.6		
		24.5	67		
		17	55.4		
	Baptiste	37.2	14.5		
		56.6	0.9		
		68.6	83.6		
		40.6	59.4		
Lime + Alum	Amisk	19.7	0		
		14.8	0		
	Crooked	11	9		
		12.9	4.2		
		11.1	0.1		
	Baptiste	6.2	4		
		57	15.9		
		55.5	6		
		74.2	1.1		
		27.5	0		

Table B-5: Electrode potentials (Eh) in mV for electrodes from cores from all three lakes pooled for both trials in Baptiste and Crooked lakes and for a single trial in Amisk Lake. Potentials are not corrected for pH or the potential of the Ag/AgCl electrode.

TIME (h)	3	4	9	10	71	72	73	170	182	194	350	374	398	422	434
Nitrogen and Earth															
	-141	-147	-189	-215	-344	-344	-440	-443	-458	-475	-461	-461	-461	-461	-461
	-209	-261	-219	-224	-421	-423	-423	-294	-296	-298	-250	-450	-452	-252	-452
	-129	-137	-179	-184	-401	-400	-402	-379	-388	-389	-436	-	-427	-427	-427
	6.6	-3.87	-48.7	-21	-376	-375	-374	-426	-441	-452	-316	433.7	-319	-324	-327
	-74.2	-48.8	-102	-99	-123	-133	45.6	-409	-420	-429	-353	-360	-354	-354	-354
	-200	-204	-286	-285	-268	-271	-272	-89	-113	-404	-496	-449	-407	-407	-407
	-149	-153	-172	-175	-368	-327	-355	-243	-277	-488	-443	-439	-434	-434	-434
	-262	-293	-302	-304	-320	-316	-318	-318	-319	-321	-357	-362	-365	-368	-473
MEAN	-145	-156	-187	-188	-328	-324	-317	-325	-339	-407	-389	-409	-402	-378	-417
SE	3.2	3.7	3.2	3.5	3.6	3.4	5.9	4.5	4.3	2.6	3.2	2.0	1.9	2.6	2.0
OXYGEN															
	74.6	74.7	69.2	66.9	82	85	94.4	250	236	225	87.4	76.7	69.6	62.6	58.3
	75.7	88.7	77.2	87.3	215	221	221	234	229	225	142	88.1	17.8	-50	-99
	14.92	5.2	-45.9	-46	217	199	208	292	289	282	-53	-149	-208	-256	-293
	-18	-36	-52	-55	-188	-186	-183	78.2	83.4	79.9	189	197	205	210	214
	135.4	169.6	143	148	255	251	254	78.2	83.4	79.9	190	197	210	214	212
	218.6	243.7	221	220	146	147	145	248	240	236	-12.7	-21	-19	-19	51.4
MEAN	8.4	9.1	6.9	7.0	121	120	123	197	193	188	9.0	6.5	4.6	2.7	2.4
SE	3.5	4.2	4.3	4.4	6.7	6.6	6.6	3.8	3.6	3.5	4.2	5.4	6.4	7.3	7.9
Iron III Chloride															
	-55.3	-76.6	113	58.3	18.1	18	17.9	46.7	45.7	44.7	38.5	37.1	35.7	34.3	33.2
	52.8	57.34	68.4	20.5	18.1	18	17.9	26.4	25.8	25.2	55.7	53.9	53.1	53.1	47.3
	108.8	121.8	24.3	54.4	49.4	49.3	49.3	45.9	45.4	45	39.2	37.5	35.5	33.2	33.2
	-185	-251	123	355	109	50.1	47.3	49.8	49.8	50	42.4	38.5	36.2	34.3	149
	56.9	57.44	61.1	36.6	41.7	41.6	145	138	124	23.6	4	-7.8	-18	-26	-89
	-32	-37.5	-37.6	48.2	146	158	148	-51	-29	-30	-211	-263	-319	-107	-107
MEAN	-9	-21	5.9	9.6	6.4	5.6	7.1	4.3	4.4	2.6	-5	-1.7	-2.9	4	1.1
SE	4.3	5.4	2.4	5.2	2.1	2.1	2.5	2.5	2.0	1.2	4.2	5.0	5.9	2.5	3.9

Table B-5: Cont'd.

Iron III Chloride + Oxygen		11.02	10.52	3.19	470	121	120	119	82.4	78.9	75.9	32.8	30	24.5	19.7	15.3
		227.3	220.5	231	454	113	113	113	-123	-149	-165	-328	-335	-334	-337	-337
		102.1	100.1	174	425	185	179	161	255	91.3	82.9	77	71.3	65.8	66.4	66.4
		168.3	182.7	111	530	390	389	388	158	153	13	130	57.7	40.2	28.5	27.1
		-166	-158	-89.3	-82	-23	-7	-2	104	102	105	102	57.4	53.8	50.7	47.6
MEAN		69	71	86	359	157	159	156	95	55	22	3	-24	-30	-34	-36
SE		69	68	58	112	67	65	64	62	53	49	84	78	76	76	76
ALUM		141	141	284	270	59.8	-215	-222	-220	-251	-265	-271	-273	-273	-273	-272
		-268	-289	-154	-147	-200	-208	-416	-410	-410	-480	-483	-485	-488	-495	-494
		-199	-207	-165	-207	-227	-211	-365	-372	-378	-538	-545	-538	-526	-513	-515
MEAN		-109	-118	-12	-28	-122	-211	-334	-334	-346	-428	-433	-432	-429	-427	-427
SE		126	132	148	150	91	2	58	58	49	83	83	81	79	77	78
LIME		-97.2	-99.4	-86	-111	-432	-434	-435	-437	-582	-587	-577	-564	-557	-548	-548
		53.4	76	76.5	71.8	-461	-461	-463	-465	-467	-485	-486	-489	-492	-495	-497
		-39.5	-42.8	-58	-78	-169	-173	-391	-394	-397	-60.7	-63	-65	-68	-67	-71
		-23.3	-30.7	-8.4	-27	-172	-173	-235	-228	-212	-245	-136	-136	-245	-136	-245
MEAN		-27	-24	-19	-36	-309	-310	-381	-381	-415	-344	-316	-314	-341	-312	-340
SE		31	37	36	40	80	79	51	53	78	119	127	125	113	123	112
LIME + ALUM		-187	-187	-151	-226	-326	-335	-371	-357	-336	-354	-360	-360	-360	-360	-360
		34.3	-2.29	-255	-299	-397	-403	-436	-430	-415	-355	-360	-355	-360	-355	-355
		-413	-411	-409	-408	-425	-425	-426	-144	-123	-108	-287	-278	-272	-264	-255
		-305	-482	-174	-71.5	-446	-441	-430	-405	-396	-387	-15	-306	-298	-290	-281
		-95.9	-99.6	-128	-97	-152	-157	-198	-206	-222	-268	-277	-277	-277	-277	-277
MEAN		-193	-236	-223	-220	-349	-352	-372	-308	-298	-294	-260	-315	-313	-309	-306
SE		78	91	51	63	53	52	45	57	55	51	64	18	20	20	22

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